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(54) Title: METALLOCENE COCATALYST

(57) Abstract

Boratabenzene cocatalysts, especially novel pentafluorophenyl boratabenzenes, are useful cocatalysts or activators with metallocenes. They are less expensive than prior art activators, are soluble and offer more irreversible reactions. Compositions comprise at least one metallocene catalyst and at least one dihydroboratabenzene or anion thereof. Processes include polymerizations with metallocenes in the presence of boratabenzene cocatalyst and activation process including bulk electrolysis techniques.

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METALLOCENE COCATALYST

This invention relates to cocatalysts or activators useful with
5 metallocene catalysts, particularly with metallocene catalysts used to make
olefin polymers.

Metallocene catalysts are well known, especially for polymerization
of olefins. The term "metallocene catalysts" is used to mean
organometallic compounds having a rare earth or transition metal in
10 coordination with members of at least one five-membered carbon
(preferably cyclopentadienyl) ring.

It is generally recognized that cocatalysts or activators are useful
with metallocene catalysts, especially in polymerization of olefins. Known
activating cocatalysts include for example polymeric or oligomeric
15 alumoxanes, especially methylalumoxane, triisobutyl aluminum modified
methylalumoxane, or diisobutylalumoxane; strong Lewis acids (the term
"strong Lewis acid" as used herein is defined as trihydrocarbyl substituted
Group 13 compounds, especially tri(hydrocarbyl)aluminum- or
tri(hydrocarbyl)boron compounds and halogenated derivatives thereof,
20 having from 1 to 10 carbons in each hydrocarbyl or halogenated
hydrocarbyl group, more especially perfluorinated tri(aryl)boron compounds,
and most especially tris(pentafluorophenyl)borane); amine, phosphine,
aliphatic alcohol and mercaptan adducts of halogenated tri(C₁₋₁₀)
hydrocarbyl)boron compounds, especially such adducts of perfluorinated
25 tri(aryl)boron compounds; nonpolymeric, ionic, compatible,
noncoordinating, activating compounds (including the use of such
compounds under oxidizing conditions); bulk electrolysis (explained in more
detail hereinafter); and combinations of the foregoing activating cocatalysts
and techniques. Preferred species include tris(pentafluorophenyl)borane
30 and the ionic activators containing the anion tetrakis

(pentafluorophenyl)borat . These compounds ar effective but require several pentafluorophenyl groups per mol cule which are difficult to obtain or synthesize and are, therefore, quite expensive. Ionic activators react irreversibly with metallocenes and therefore may be preferred over the 5 neutral strong Lewis acid activators, which may react reversibly with a metallocene. However, a commercial drawback of these ionic activators is their poor solubility in the polymerization medium, that is, hydrocarbon solvents.

It would be desirable to have activators or cocatalysts which retain 10 good solubility in hydrocarbon solvents and are preferably less likely to result in reversible reactions and/or which are less expensive, that is use less of the difficult to obtain pentafluorophenyl group.

Boratabenzenes are known and have been used as ligands but are not used as cocatalysts, activators or counterions for metallocene 15 catalysts.

The boratabenzenes are anionic species which are boron containing analogues to benzene. They are previously known in the art having been described by G. Herberich, et al., in Organometallics, 14,1, 471-480 (1995). They may be prepared by reaction of stannocyclohexadiene and a 20 borontrihalide followed by substitution with a hydrocarbyl group.

It has now been found that cocatalysts or activators comprising hydroboratabenzenes or boratabenzene anions, preferably as the neutral 1,4-dihydroboratabenzene, are useful in polymerization of olefins using 25 metallocene catalysts. Boratabenzene cocatalysts advantageously involve fewer pentafluorophenyl groups than preferred trispentafluorophenyl borane and salts containing tetrakis(pentafluorophenyl) borates, respectively. Furthermore, 1,4-dihydroboratabenzenes are advantageously involved in less reversible reactions with metallocenes.

- The present invention includes a process of polymerizing olefins using metallocene catalysts in the presence of at least one activator comprising a 1,4-dihydroboratabenzene or boratabenzene (collectively boratabenzene cocatalysts) as well as a process for polymerizing olefins
- 5 using at least one metallocene catalyst wherein the catalyst is activated by at least one activator comprising a boratabenzene.

The invention also includes supporting electrolyte compositions, especially for bulk electrolysis activating techniques, comprising boratabenzenes.

- 10 Further, the invention includes a composition of matter comprising at least one metallocene catalyst and at least one cocatalyst comprising a boratabenzene and compositions of matter comprising the resulting cationic metallocene catalysts and anionic boratabenzene counterions preferably which arise from the reaction of metallocenes in the +4 oxidation state
- 15 with a cocatalyst comprising a boratabenzene.

Additionally, the invention includes perfluorophenyl hydroborabenzenes of Formula 1 wherein R' is a pentafluorobenzene group, especially 1-pentafluorophenyl-1,4-dihydroboratabenzene [C₅H₆B-C₆F₅] and the anion thereof, [C₅H₅B-C₆F₅]⁻.

- 20 Additional components in the compositions of the invention include trialkylaluminum and/or methylalumoxanes or derivatives, thereof, for example triisopropylaluminum modified methylaluminoxane. Also included in the invention are reaction products of the compositions of the invention especially those formed under reaction (polymerization)
- 25 conditions.

Figure 1 is an illustrative equation of the invention using a boratabenzene as a cocatalyst to form a cationic metallocene catalyst.

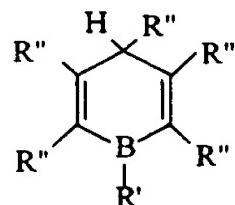
- Figure 2 is an illustrative equation of the invention using [NHR₃]
- 30 [C₅H₅BR'] as the activating species.

Figure 3 is an illustrative equation of the invention using a strong Lewis acid cationic activator.

These examples are non-limiting and it is understood that metallocenes in the +3 or +2 oxidation state can react differently with a 5 boratabenzene cocatalyst.

The term activator or cocatalyst is used herein to refer compounds which, when combined with a metallocene, result in a more active catalyst than the same metallocene would have been without the activator. The 10 activators of the present invention fall into two classes: 1) The neutral 1,4-dihydroboratabenzene, Formula 1. 2) Salts containing the boratabenzene anion, Formula 2. The acidity of the protons in the 4 position of the 1,4-dihydroboratabenzenes render this class of compounds especially reactive towards metallocenes. An illustrative, but non-limiting, 15 example of activation using a complex of Formula 1 is shown in figure 1, where a compound of Formula 1 is involved in a protonysis reaction with a metallocene with liberation of methane. An illustrative, but non-limiting, example of activation using a complex of formula 2 is shown in figure 2, where a compound of Formula 2 is involved in a protonysis reaction with 20 a metallocene with liberation of methane.

1,4-Dihydroboratabenzenes (hereinafter also referred to as hydroboratabenzenes or collectively with boratabenzene anions as boratabenzene cocatalysts) are compounds of Formula I:



wherein R' is a hydrocarbyl group, silylhydrocarbyl, perfluorohydrocarbyl group, dialkylamido group or halide (Cl, Br, I or F, preferably Cl, Br or F more preferably F). The hydrocarbyl group, is linear, branched, cyclic, aromatic, alkyl aromatic, or arylalkyl and is unsubstituted or inertly substituted and preferably has less than 24 carbon atoms, more preferably from 1 to 24, most preferably from 1 to 12 carbon atoms, particularly preferably 6 carbon atoms, especially an unsubstituted or inertly substituted phenyl ring. Inertly substituted means having substituents which do not undesirably interfere with the function of the cocatalyst in activation of the metallocene catalyst or the catalytic activity of the resulting activated catalyst. Such inert substituents include halogen atoms (Cl, Br, I, or F, more preferably Cl, Br, F, most preferably F), nitrogen-containing groups not having active hydrogen such as tertiary amine or amide groups, silyl groups, ether oxygen, and hydrocarbyl, 15 perhalohydrocarbyl preferably pentafluorophenyl. Preferred hydrocarbyl groups include unsubstituted and fluoro substituted hydrocarbyl groups which are electron withdrawing in nature. The alkyl groups on dialkylamido groups are the same or different from one another and are independently unsubstituted or inertly substituted as the hydrocarbyl groups and 20 preferably each have from 1 to 24, preferably from 1 to 12, most preferably from 1 to 6 carbon atoms. Each R' independently optionally is or comprises D, a linking group described hereinafter.

Each R" is independently H, or an unsubstituted or inertly substituted hydrocarbyl, silylhydrocarbyl, perfluorocarbyl, alkoxide or dihydrocarbyl 25 amido group. Each carbon-containing group is as described for R' and preferably has from 1 to 12 carbon atoms (for a total of preferably less than 24 carbon atoms for the dialkylamido group). Two or more R" or R' and at least one R" are optionally joined into a ring or rings which are suitably aromatic, alkyl, or heteroatom containing rings or combinations thereof. Preferably all R" are H for ease of synthesis. For delocalizing the 30

negative charge, each R" is preferably selected from fluorine, fluorohydrocarbyl, fluorocarbyl, chlorine, more preferably fluorine or fluorine-containing groups. Bulky hydrocarbyl groups, such as tertiary butyl, are also desirable R" groups as these groups often help render the

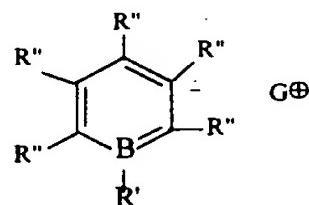
5 boratabenzene anion non-coordinating. Each R" independently optionally is or comprises D, a linking group described hereinafter.

Advantageously, R' and R" are preferably selected to delocalize negative charge and thus stabilize the corresponding anion. Any R" which is not hydrogen is preferably ortho or para, more preferably para to the

10 boron atom of the boratabenzene ring.

Compounds of Formula 1 are known to form anions of Formula 2 readily because of the acidity of the hydrogen atom. Acidity is increased by substitution which increases the ability of the boratabenzene ring to delocalize negative charge. Formula 2:

15



wherein R' and R" are as defined for Formula 1. For use in the practice of the current invention the boratabenzene anion of formula 2 is associated

20 with a cation G⁺. In one embodiment of this invention G⁺ is the cation of an ionic activator. In this embodiment G⁺ is preferably [NHR₃]⁺, [NR₄]⁺, [SiR₃]⁺, [CPh₃]⁺, or [(C₅H₅)₂Fe]⁺ or Ag⁺, where R is independently in each occurrence a hydrocarbyl, silylhydrocarbyl, or perfluorocarbyl of from 1 to 24 carbons, more preferably from 1 to 12 carbons arranged in a linear, branched, or ring structure. Ph is phenyl. In a preferred embodiment [NHR₃]⁺ is [NH(CH₃)(C₁₈H₃₇)₂]⁺.

In the second embodiment of this invention G⁺ is a cation arising from the reaction of a metallocene with a 1,4-dihydroboratabenzene of Formula 1. In this embodiment G⁺ may be either the metallocene cation or a cationic species arising from a subsequent reaction.

- 5 Illustrative, but non-limiting, examples of 1,4-dihydroboratabenzene cocatalysts of Formula 1 are 1-phenyl-1,4-dihydroboratabenzene; 1-methyl-1,4-dihydroboratabenzene; 1-ethyl-1,4-dihydroboratabenzene; 1-pentafluorophenyl-1,4-dihydroboratabenzene; 1-dimethylamido-1,4-dihydroboratabenzene; 1-neopentyl-1,4-dihydroboratabenzene; 1-tbutyl-10 1,4-dihydroboratabenzene; 1-trimethylsilyl-1,4-dihydroboratabenzene; 1-trimethylsilylmethyl-1,4-dihydroboratabenzene; 1-fluoro-1,4-dihydroboratabenzene; 1-(3,5-bis-trifluoromethyl-phenyl)-1,4-dihydroboratabenzene; 1-phenyl-4-methyl-1,4-dihydroboratabenzene; 1-methyl-4-methyl-1,4-dihydroboratabenzene; 15 1-pentafluorophenyl-4-methyl-1,4-dihydroboratabenzene; 1-dimethylamido-4-methyl-1,4-dihydroboratabenzene; 1-neopentyl-4-methyl-1,4-dihydroboratabenzene; 1-tbutyl-4-methyl-1,4-dihydroboratabenzene; 1-trimethylsilyl-4-methyl-1,4-dihydroboratabenzene; 1-trimethylsilylmethyl-4-methyl-1,4-dihydroboratabenzene; 1-fluoro-4-methyl-1,4-dihydroboratabenzene; 1-(3,5-bis-trifluoromethyl-phenyl)-4-methyl-1,4-dihydroboratabenzene; 1-phenyl-4-tbutyl-1,4-dihydroboratabenzene; 1-methyl-4-tbutyl-1,4-dihydroboratabenzene; 1-ethyl-4-tbutyl-1,4-dihydroboratabenzene; 1-pentafluorophenyl-4-tbutyl-1,4-dihydroboratabenzene; 1-dimethylamido-4-tbutyl-1,4-dihydroboratabenzene; 1-neopentyl-4-tbutyl-1,4-dihydroboratabenzene; 1-tbutyl-4-tbutyl-1,4-dihydroboratabenzene; 1-trimethylsilyl-4-tbutyl-1,4-dihydroboratabenzene; 1-trimethylsilylmethyl-4-tbutyl-1,4-dihydroboratabenzene; 1-fluoro-4-tbutyl-1,4-dihydroboratabenzene; 1-(3,5-bis-trifluoromethyl-phenyl)-4-tbutyl-1,4-dihydroboratabenzene; 30 1-phenyl-2,4-dimethyl-1,4-dihydroboratabenzene;

- 1,2,4-trimethyl-1,4-dihydroboratabenzene; 1-ethyl-2,4-dimethyl-1,4-dihydroboratabenzene; 1-pentafluorophenyl-2,4-dimethyl-1,4-dihydroboratabenzene; 1-dimethylamido-2,4-dimethyl-1,4-dihydroboratabenzene; 1-neopentyl-2,4-dimethyl-1,4-dihydroboratabenzene; 1-tbutyl-2,4-dimethyl-1,4-dihydroboratabenzene; 1-trimethylsilyl-2,4-dimethyl-1,4-dihydroboratabenzene; 1-trimethylsilylmethyl-2,4-dimethyl-1,4-dihydroboratabenzene; 1-fluoro-2,4-dimethyl-1,4-dihydroboratabenzene; 1-(3,5-bis-trifluoromethyl-phenyl)-2,4-dimethyl-1,4-dihydroboratabenzene; 1-phenyl-2-methoxide-4-tbutyl-1,4-dihydroboratabenzene; 1-methyl-2-methoxide-4-tbutyl-1,4-dihydroboratabenzene; 1-ethyl-2-methoxide-4-tbutyl-1,4-dihydroboratabenzene; 1-pentafluorophenyl-2-methoxide-4-tbutyl-1,4-dihydroboratabenzene; 1-dimethylamido-2-methoxide-4-tbutyl-1,4-dihydroboratabenzene; 1-neopentyl-2-methoxide-4-tbutyl-1,4-dihydroboratabenzene; 1-tbutyl-2-methoxide-4-tbutyl-1,4-dihydroboratabenzene; 1-trimethylsilyl-2-methoxide-4-tbutyl-1,4-dihydroboratabenzene; 1-trimethylsilylmethyl-2-methoxide-4-tbutyl-1,4-dihydroboratabenzene; 1-fluoro-2-methoxide-4-tbutyl-1,4-dihydroboratabenzene; 1-(3,5-bis-trifluoromethyl-phenyl)-2-methoxide-4-tbutyl-1,4-dihydroboratabenzene; 1-phenyl-4-tbutyl-6-trimethylsilyl-1,4-dihydroboratabenzene; 1-methyl-4-tbutyl-6-trimethylsilyl-1,4-dihydroboratabenzene; 1-ethyl-4-tbutyl-6-trimethylsilyl-1,4-dihydroboratabenzene; 1-pentafluorophenyl-4-tbutyl-6-trimethylsilyl-1,4-dihydroboratabenzene; 1-dimethylamido-4-tbutyl-6-trimethylsilyl-1,4-dihydroboratabenzene; 1-neopentyl-4-tbutyl-6-trimethylsilyl-1,4-dihydroboratabenzene; 1-tbutyl-4-tbutyl-6-trimethylsilyl-1,4-dihydroboratabenzene; 1-trimethylsilyl-4-tbutyl-6-trimethylsilyl-1,4-dihydroboratabenzene; 1-trimethylsilylmethyl-4-tbutyl-6-trimethylsilyl-1,4-dihydroboratabenzene; 1-fluoro-4-tbutyl-6-trimethylsilyl-1,4-dihydroboratabenzene; 1-(3,5-bis-trifluoromethyl-phenyl)-4-tbutyl-6-dihydroboratabenzene;

trimethylsilyl-1,4-dihydroboratabenzene; 1-phenyl-2-diethylamido-4-^tbutyl-1,4-dihydroboratabenzene; 1-methyl-2-diethylamido-4-^tbutyl-1,4-dihydroboratabenzene; 1-ethyl-2-diethylamido-4-^tbutyl-1,4-dihydroboratabenzene; 1-pentafluorophenyl-2-diethylamido-4-^tbutyl-1,4-dihydroboratabenzene; 1-dimethylamido-2-diethylamido-4-^tbutyl-1,4-dihydroboratabenzene; 1-neopentyl-2-diethylamido-4-^tbutyl-1,4-dihydroboratabenzene; 1-^tbutyl-2-diethylamido-4-^tbutyl-1,4-dihydroboratabenzene; 1-trimethylsilyl-2-diethylamido-4-^tbutyl-1,4-dihydroboratabenzene; 1-trimethylsilylmethyl-2-diethylamido-4-^tbutyl-1,4-dihydroboratabenzene; 1-fluoro-2-diethylamido-4-^tbutyl-1,4-dihydroboratabenzene; 1-(3,5-bis-trifluoromethyl-phenyl)-2-diethylamido-4-^tbutyl-1,4-dihydroboratabenzene; 1-phenyl-4-pentafluorophenyl-1,4-dihydroboratabenzene; 1-methyl-4-pentafluorophenyl-1,4-dihydroboratabenzene; 1-ethyl-4-pentafluorophenyl-1,4-dihydroboratabenzene; 1-4-bispentafluorophenyl-1,4-dihydroboratabenzene; 1-dimethylamido-4-pentafluorophenyl-1,4-dihydroboratabenzene; 1-neopentyl-4-pentafluorophenyl-1,4-dihydroboratabenzene; 1-^tbutyl-4-pentafluorophenyl-1,4-dihydroboratabenzene; 1-trimethylsilyl-4-pentafluorophenyl-1,4-dihydroboratabenzene; 1-trimethylsilylmethyl-4-pentafluorophenyl-1,4-dihydroboratabenzene; 1-fluoro-4-pentafluorophenyl-1,4-dihydroboratabenzene; and 1-(3,5-bis-trifluoromethyl-phenyl)-4-pentafluorophenyl-1,4-dihydroboratabenzene, and mixtures thereof.

Illustrative, but non-limiting, examples of ionic cocatalysts of formula 2, containing the anionic derivatives of the aforementioned 1,4-dihydroboratabenzene are tri^tbutylammonium salts; tripropylammonium salts; tri^tbutylammonium salts; triethylammonium salts; trimethylammonium salts; N, N-dimethylanilinium salts; N, N-diethylanilinium salts; triphenylcarbenium salts; Ag salts; ferrocenium salts; tetra^tbutylammonium salts; tetrapropylammonium salts;

tetra^tbutylammonium salts; tetraethylammonium salts; tetramethylammonium salts; tetraⁿbutylsilylium salts; tetrapropylsilylium salts; tetra^tbutylsilylium salts; tetraethylsilylium salts; and tetramethylsilylium salts.

- 5 Of these compounds, preferred species of Formula 1 and 2 are those wherein R' is aromatic, preferably phenyl, most preferably perfluorophenyl. Alternatively R' is preferably fluorohydrocarbyl preferably perfluorohydrocarbyl. Of these, the preferred species are 1-perfluorophenyl-1,4-dihydroboratabenzene, [C₅H₅B-C₆F₅] and the corresponding anion [C₅H₅B-C₆F₅]⁻, compounds of Formulas 1 and 2 respectively wherein R' is perfluorophenyl and all R" are H. These compounds are novel compounds preferred in the practice of the invention because of their ability to stabilize the anion by delocalizing an the negative charge.
- 10 15 These boratabenzene cocatalysts are useful to activate metallocene catalysts, including constrained geometry catalysts.
- 15 Synthesis of hydroboratabenzene and boratabenzene salts are within the skill in the art such as illustrated by Ashe, et al. J. Amer. Chem. Soc., 1971, 93, 1804-1805 (the nomenclature of which is followed herein); Hoic, et al., J. Amer. Chem. Soc., 1995, 117, 8480-8481; Herberich, G. E. in Comprehensive Organo-Metallic Chemistry, Wilkinson, Stone and Abel, Pergamon, New York, Vol. 1, pages 392-409, 1982 and Herberich, et al., Organometallics, 1995, 14, 471-480 which are . In a preferred synthesis, an optionally substituted 1,4-diacetylene, for example ≡ -CH₂ - ≡ is reacted with a dialkyltinhydride, for example (n-C₄H₉)₂SnH₂), to form the corresponding dihydrodialkylstannobenzene which is reacted with an organoborondibromide, for example phenylboron dibromide. To form a substituted species, for example the preferred pentafluorophenyl boratabenzene, a correspondingly substituted organoboron dibromide, for example pentafluorophenylboron dibromide is used. Substitution on the
- 20 25 30

boratabenzene ring is achieved by use of a substituted 1,5-diacetylene or, alternatively, by reactions within the skill in the art on a boratabenzene ring or the dihydrodialkylstannabenzene. Alternatively, substituted 2,4-pentadienylboranes are used as starting materials in the synthesis disclosed
5 by Herberich, et al.

Metallocene complexes are advantageously rendered catalytically active by combination with one or more activating cocatalysts, by use of an activating technique, or a combination thereof. Activating cocatalysts and activating techniques have been previously taught with respect to different
10 metal complexes in the following references: EP-A-277,003, US-A-5,153,157, US-A-5,064,802, EP-A-468,651 (equivalent to U.S. Serial No. 07/547,718), EP-A-520,732 (equivalent to U.S. Serial No. 07/876,268), and EP-A-520,732 (equivalent to U.S. Serial No. 07/884,966 filed May 1,
15 1992). It is recognized by those skilled in the art that admixtures of metallocene catalysts and boratabenzenes may result in interactions between the molecular species present. The result of such interactions are referred to herein as interaction products, whatever form the interactions take, for instance chemical reactions, ionic reactions solvation and the like.

Practice of the invention is applicable to any metallocene catalyst
20 within the skill in the art. In a preferred embodiment, at least one metallocene component comprises bridged, biscyclopentadienyl, Group 4, 5, or 6 transition metal, and Lanthanides. Preferred metallocenes include bridged bisindenyl, Group 4 dihalide, dihydrocarbyl and diene derivatives. When dihalide metallocenes are used in the present invention they are
25 advantageously first contacted with at least one trihydrocarbyl aluminum or alumoxane species prior to reaction with a boratabenzene cocatalyst. Specific metallocene catalysts known in the art are discussed in such references as EPA Nos. 485,820; 485,821; 485,822; 485,823; 518,092; and 519,237; U.S. Pat. Nos. 5,145,819; 5,296,434.

All references herein to elements or metals belonging to a certain Group refer to the Periodic Table of the Elements published and copyrighted by CRC Press, Inc., 1989. Also any reference to the Group or Groups shall be to the Group or Groups as reflected in this Periodic Table of the Elements

5 using the IUPAC system for numbering groups.

Advantageous catalysts for use herein are advantageously derivatives of any transition metal including Lanthanides, but preferably of Group 3, 4, or Lanthanide metals which are in the +2, +3, or +4 formal oxidation state. Preferred compounds include metal complexes containing from 1 to

10 3 π -bonded anionic or neutral ligand groups, which are optionally cyclic or non-cyclic delocalized π -bonded anionic ligand groups. Exemplary of such π -bonded anionic ligand groups are conjugated or nonconjugated, cyclic or non-cyclic dienyl groups, and allyl groups. By the term " π -bonded" is meant that the ligand group is bonded to the transition metal by means of its
15 delocalized π electrons.

Each atom in the delocalized π -bonded group is optionally independently substituted with a radical selected from the group consisting of hydrogen, halogen, hydrocarbyl, halohydrocarbyl, hydrocarbyl-substituted metalloid radicals wherein the metalloid is selected from Group 14 of the
20 Periodic Table of the Elements, and such hydrocarbyl- or hydrocarbyl- substituted metalloid radicals further substituted with a Group 15 or 16 hetero atom containing moiety. Included within the term "hydrocarbyl" are C₁₋₂₀ straight, branched and cyclic alkyl radicals, C₆₋₂₀ aromatic radicals, C₇₋₂₀ alkyl-substituted aromatic radicals, and C₇₋₂₀ aryl-substituted alkyl
25 radicals. In addition two or more such adjacent radicals may together form a fused ring system, a hydrogenated fused ring system, or a metallocycle with the metal. Suitable hydrocarbyl-substituted organometalloid radicals include mono-, di- and tri-substituted organometalloid radicals of Group 14 elements wherein each of the hydrocarbyl groups contains from 1 to 20
30 carbon atoms. Examples of advantageous hydrocarbyl-substituted organo-

metalloid radicals include trimethylsilyl, triethylsilyl, ethyldimethylsilyl, methyltriethylsilyl, triphenylgermyl, and trimethylgermyl groups. Examples of Group 15 or 16 hetero atom containing moieties include amine, phosphine, ether or thioether moieties or monovalent derivatives thereof, e.g. amide, phosphide, ether or thioether groups bonded to the transition metal or Lanthanide metal, and bonded to the hydrocarbyl group or to the hydrocarbyl-substituted metalloid containing group.

- 5 Examples of advantageous anionic, delocalized π -bonded groups include cyclopentadienyl, indenyl, fluorenyl, tetrahydroindenyl, tetrahydro-
10 fluorenyl, octahydrofluorenyl, pentadienyl, cyclohexadienyl, dihydroanthracenyl, hexahydroanthracenyl, and decahydroanthracenyl groups, as well as C1-10 hydrocarbyl-substituted or C1-10 hydrocarbyl-substituted silyl substituted derivatives thereof. Preferred anionic delocalized π -bonded groups are cyclopentadienyl,
15 pentamethylcyclopentadienyl, tetramethylcyclopentadienyl, tetramethylsilylcyclopentadienyl, indenyl, 2,3-dimethylindenyl, fluorenyl, 2-methylindenyl, 2-methyl-4-phenylinenyl, tetrahydrofluorenyl, octahydrofluorenyl, and tetrahydroindenyl.

- A preferred class of catalysts are transition metal complexes
20 corresponding to the Formula A:

$L_1MX_mX'_nX''_p$, or a dimer thereof

wherein:

- L is an anionic, delocalized, π -bonded group that is bound to M, containing up to 50 non-hydrogen atoms, optionally two L groups may be joined together forming a bridged structure, and further optionally one L is bound to X;
25

M is a metal of Group 4 of the Periodic Table of the Elements in the +2, +3 or +4 formal oxidation state;

- X is an optional, divalent substituent of up to 50 non-hydrogen atoms
30 that together with L forms a metallocycle with M;

X' at each occurrence is an optional neutral Lewis base having up to 20 non-hydrogen atoms;

X" each occurrence is a monovalent, anionic moiety having up to 40 non-hydrogen atoms, optionally, two X" groups are covalently bound

- 5 together forming a divalent dianionic moiety having both valences bound to M, or, optionally 2 X" groups are covalently bound together to form a neutral, conjugated or nonconjugated diene that is π -bonded to M (whereupon M is in the +2 oxidation state), or further optionally one or more X" and one or more X' groups are bonded together thereby forming a
- 10 moiety that is both covalently bound to M and coordinated thereto by means of Lewis base functionality;

/ is 0, 1 or 2;

m is 0 or 1;

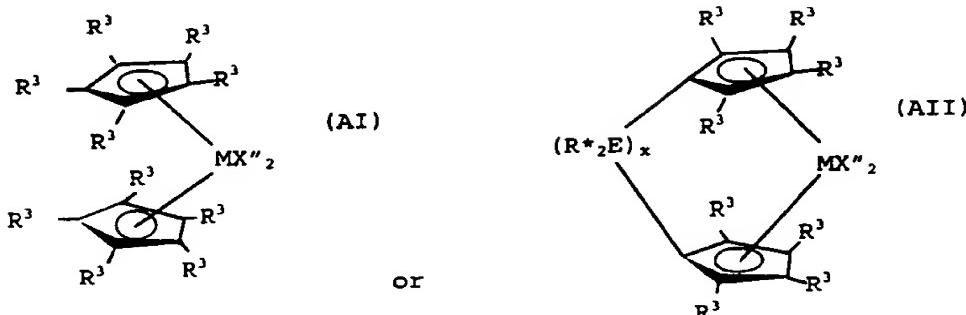
n is a number from 0 to 3;

- 15 p is an integer from 0 to 3; and

the sum, / + m + p, is equal to the formal oxidation state of M, except when 2 X" groups together form a neutral conjugated or non-conjugated diene that is π -bonded to M, in which case the sum / + m is equal to the formal oxidation state of M.

- 20 Preferred complexes include those containing either one or two L groups. The latter complexes include those containing a bridging group linking the two L groups. Preferred bridging groups are those corresponding to the formula $(ER^*)_2x$ wherein E is silicon, germanium, tin, or carbon, R* independently each occurrence is hydrogen or a group
- 25 selected from silyl, hydrocarbyl, hydrocarbyloxy and combinations thereof, said R* having up to 30 carbon or silicon atoms, and x is 1 to 8. Preferably, R* independently each occurrence is methyl, ethyl, propyl, benzyl, tert-butyl, phenyl, methoxy, ethoxy or phenoxy.

Examples of the complexes containing two L groups are compounds corresponding to the formula:



5 wherein:

M is titanium, zirconium or hafnium, preferably zirconium or hafnium, in the + 2 or + 4 formal oxidation state;

10 R^3 in each occurrence independently is selected from the group consisting of hydrogen, hydrocarbyl, silyl, germyl, cyano, halo and combinations thereof, said R^3 having up to 20 non-hydrogen atoms, or adjacent R^3 groups together form a divalent derivative (for example, a hydrocarbadiyl, germadiyl group) thereby forming a fused ring system, and

15 X'' independently each occurrence is an anionic ligand group of up to 40 non-hydrogen atoms, or two X'' groups together form a divalent anionic ligand group of up to 40 non-hydrogen atoms or together are a conjugated diene having from 4 to 30 non-hydrogen atoms forming a π -complex with M, whereupon M is in the + 2 formal oxidation state, and

20 R^* , E and x are as previously defined.

The foregoing metal complexes are especially suited for the preparation of polymers having stereoregular molecular structure. In such capacity it is preferred that the complex possesses C_s symmetry or possesses a chiral, stereorigid structure. Examples of the first type are compounds possessing different delocalized π -bonded systems, such as one cyclopentadienyl group and one fluorenyl group. Similar systems based on 25 Ti(IV) or Zr(IV) were disclosed for preparation of syndiotactic olefin

polymers in Ewen, et al., J. Am. Chem. Soc. 110, 6255-6256 (1980). Examples of chiral structures include rac bis-indenyl complexes. Similar systems based on Ti(IV) or Zr(IV) were disclosed for preparation of isotactic olefin polymers in Wild et al., J. Organomet. Chem., 232, 233-47, (1982).

- 5 Exemplary bridged ligands containing two π -bonded groups are:
(dimethylsilyl-bis(cyclopentadienyl)), (dimethylsilyl-
bis(methylcyclopentadienyl)), (dimethylsilyl-bis(ethylcyclopentadienyl)),
(dimethylsilyl-bis(t-butylcyclopentadienyl)), (dimethylsilyl-
bis(tetramethylcyclopentadienyl)), (dimethylsilyl-bis(indenyl)), (dimethylsilyl-
10 bis(tetrahydroindenyl)), (dimethylsilyl-bis(fluorenyl)), (dimethylsilyl-
bis(tetrahydrofluorenyl)), (dimethylsilyl-bis(2-methyl-4-phenylindenyl)),
(dimethylsilyl-bis(2-methylindenyl)), (dimethylsilyl-cyclopentadienyl-
fluorenyl), (dimethylsilyl-cyclopentadienyl-octahydrofluorenyl),
(dimethylsilyl-cyclopentadienyl-tetrahydrofluorenyl), (1, 1, 2, 2-tetramethyl-
15 1, 2-disilyl-bis-cyclopentadienyl), (1, 2-bis(cyclopentadienyl)ethane, and
(isopropylidene-cyclopentadienyl-fluorenyl).

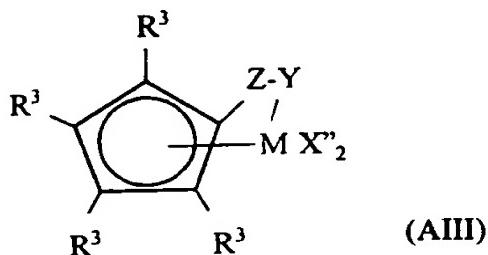
- Preferred X" groups are selected from hydride, hydrocarbyl, silyl,
germyl, halohydrocarbyl, halosilyl, silylhydrocarbyl and aminohydrocarbyl
groups, or two X" groups together form a divalent derivative of a
20 conjugated diene or else together they form a neutral, π -bonded, conjugated
diene. Most preferred X" groups are C₁-20 hydrocarbyl groups, including
those optionally formed from two X" groups together.

- A further class of metal complexes utilized in the present invention
corresponds to the preceding formula L₁MX_mX'_nX"_p, or a dimer thereof.
25 wherein X is a divalent substituent of up to 50 non-hydrogen atoms that
together with L forms a metallocycle with M.

- Preferred divalent X substituents include groups containing up to 50
non-hydrogen atoms comprising at least one atom that is oxygen, sulfur,
boron or a member of Group 14 of the Periodic Table of the Elements
30 directly attached to the delocalized π -bonded group, and a different atom,

selected from the group consisting of nitrogen, phosphorus, oxygen or sulfur that is covalently bonded to M.

A preferred class of such Group 4 metal coordination complexes used according to the present invention corresponds to the formula:



5

wherein:

M is titanium or zirconium in the +2 or +4 formal oxidation state;

X'' and R³ are as previously defined for formulas A1 and A11;

Y is -O-, -S-, -NR*-, -PR*-; and

10 Z is SiR*₂, CR*₂, SiR*₂SiR*₂, CR*₂CR*₂, CR* = CR*,

CR*₂SiR*₂, or GeR*₂, wherein R* is as previously defined.

Illustrative Group 4 metal complexes that may be employed in the practice of the present invention include:

cyclopentadienyltitaniumtrimethyl, cyclopentadienyltitaniumtriethyl,

15 cyclopentadienyltitaniumtriisopropyl, cyclopentadienyltitaniumtriphenyl,

cyclopentadienyltitaniumtribenzyl, cyclopentadienyltitanium-2,4-

dimethylpentadienyl, cyclopentadienyltitanium-2,4-dimethylpentadienyl-

triethylphosphine, cyclopentadienyltitanium-2,4-dimethylpentadienyl-

trimethylphosphine, cyclopentadienyltitaniumdimethylmethoxide,

20 cyclopentadienyltitaniumdimethylchloride,

pentamethylcyclopentadienyltitaniumtrimethyl, indenyltitaniumtrimethyl,

indenyltitaniumtriethyl, indenyltitaniumtripropyl, indenyltitaniumtriphenyl,

tetrahydroindenyltitaniumtribenzyl,

pentamethylcyclopentadienyltitaniumtriisopropyl,

25 pentamethylcyclopentadienyltitaniumtribenzyl,

pentamethylcyclopentadienyltitaniumdimethylmethoxide,

- pentamethylcycl pentadienyltitaniumdimethylchloride,
bis(η^5 -2,4-dimethylpentadienyl)titanium,
bis(η^5 -2,4-dimethylpentadienyl)titanium-trimethylphosphine,
bis(η^5 -2,4-dimethylpentadienyl)titanium-triethylphosphine,
- 5 octahydrofluorenyltitaniumtrimethyl, tetrahydroindenyltitaniumtrimethyl,
tetrahydrofluorenyltitaniumtrimethyl, (tert-butylamido)(1,1-dimethyl-
2,3,4,9,10- η -1,4,5,6,7,8-
hexahydronaphthalenyl)dimethylsilanetitaniumdimethyl,
(tert-butylamido)(1,1,2,3-tetramethyl-2,3,4,9,10- η -1,4,5,6,7,8-
- 10 hexahydronaphthalenyl)dimethylsilanetitaniumdimethyl, (tert-
butylamido)(tetramethyl- η^5 -cyclopentadienyl) dimethylsilanetitanium
dibenzyl,
(tert-butylamido)(tetramethyl- η^5 -cyclopentadienyl)dimethylsilanetitanium
dimethyl, (tert-butylamido)(tetramethyl- η^5 -cyclopentadienyl)-1,2-
- 15 ethanediyltitanium dimethyl, (tert-butylamido)(tetramethyl- η^5 -
indenyl)dimethylsilanetitanium dimethyl, (tert-butylamido)(tetramethyl- η^5 -
cyclopentadienyl)dimethylsilane titanium (III) 2-(dimethylamino)benzyl;
(tert-butylamido)(tetramethyl- η^5 -cyclopentadienyl)dimethylsilanetitanium
(III) allyl, (tert-butylamido)(tetramethyl- η^5 -
- 20 cyclopentadienyl)dimethylsilanetitanium (III) 2,4-dimethylpentadienyl, (tert-
butylamido)(tetramethyl- η^5 -cyclopentadienyl)dimethyl-silanetitanium (II)
1,4-diphenyl-1,3-butadiene,
(tert-butylamido)(tetramethyl- η^5 -cyclopentadienyl)dimethyl-silanetitanium
(II) 1,3-pentadiene, (tert-butylamido)(2-methylindenyl)dimethylsilanetitanium
- 25 (II) 1,4-diphenyl-1,3-butadiene, (tert-butylamido)(2-
methylindenyl)dimethylsilanetitanium (II) 2,4-hexadiene, (tert-butylamido)(2-
methylindenyl)dimethylsilanetitanium (IV) 2,3-dimethyl-1,3-butadiene,
(tert-butylamido)(2-methylindenyl)dimethylsilanetitanium (IV) isoprene,
(tert-butylamido)(2-methylindenyl)dimethylsilanetitanium 1,3-butadiene,
- 30 (tert-butylamido)(2,3-dimethylindenyl)dimethylsilanetitanium (IV) 2,3-

- dimethyl-1,3-butadiene, (tert-butylamido)(2,3-dimethylindenyl)dimethylsilanetitanium (IV) isoprene; (tert-butylamido)(2,3-dimethylindenyl)dimethylsilanetitanium (IV) dimethyl; (tert-butylamido)(2,3-dimethylindenyl)dimethylsilanetitanium (IV) dibenzyl; (tert-butylamido)(2,3-dimethylindenyl)dimethylsilanetitanium 1,3-butadiene, (tert-butylamido)(2,3-dimethylindenyl)dimethylsilanetitanium (II) 1,3-pentadiene, (tert-butylamido)(2,3-dimethylindenyl)dimethylsilanetitanium (II) 1,4-diphenyl-1,3-butadiene, (tert-butylamido)(2-methylindenyl)dimethylsilanetitanium (II) 1,3-pentadiene, (tert-butylamido)(2-methylindenyl)dimethylsilanetitanium (IV) dimethyl, (tert-butylamido)(2-methylindenyl)dimethylsilanetitanium (IV) dibenzyl, (tert-butylamido)(2-methyl-4-phenylindenyl)dimethylsilanetitanium (II) 1,4-diphenyl-1,3-butadiene, (tert-butylamido)(2-methyl-4-phenylindenyl)dimethylsilanetitanium (II) 1,3-pentadiene, (tert-butylamido)(2-methyl-4-phenylindenyl)dimethylsilanetitanium (II) 2,4-hexadiene, (tert-butylamido)(tetramethyl- η^5 -cyclopentadienyl)dimethylsilanetitanium 1,3-butadiene, (tert-butylamido)(tetramethyl- η^5 -cyclopentadienyl)dimethylsilanetitanium (IV) 2,3-dimethyl-1,3-butadiene, (tert-butylamido)(tetramethyl- η^5 -cyclopentadienyl)dimethylsilanetitanium (IV) isoprene, (tert-butylamido)(tetramethyl- η^5 -cyclopentadienyl)dimethylsilanetitanium (II) 1,4-dibenzyl-1,3-butadiene, (tert-butylamido)(tetramethyl- η^5 -cyclopentadienyl)dimethylsilanetitanium (II) 2,4-hexadiene, (tert-butylamido)(tetramethyl- η^5 -cyclopentadienyl)dimethylsilanetitanium (II) 3-methyl-1,3-pentadiene, (tert-butylamido)(2,4-dimethylpentadien-3-yl)dimethylsilanetitaniumdimethyl, (tert-butylamido)(6,6-dimethylcyclohexadienyl)dimethylsilanetitaniumdimethyl, (tert-butylamido)(1,1-dimethyl-2,3,4,9,10- η -1,4,5,6,7,8-hexahydronaphthalen-4-yl)dimethylsilanetitaniumdimethyl, (tert-butylamido)(1,1,2,3-tetramethyl-2,3,4,9,10- η -1,4,5,6,7,8-hexahydronaphthalen-4-yl)dimethylsilanetitaniumdimethyl(tert-butylamido)(tetramethyl- η^5 -

- cyclopentadienyl methylphenyl-silanetitanium (IV) dimethyl,
(tert-butylamido)(tetramethyl- η^5 -cyclopentadienyl methylphenyl-
silanetitanium (II) 1,4-diphenyl-1,3-butadiene, 1-(tert-butylamido)-2-
(tetramethyl- η^5 -cyclopentadienyl)ethanediyl-titanium (IV) dimethyl, and 1-
5 (tert-butylamido)-2-(tetramethyl- η^5 -cyclopentadienyl)ethanediyl-titanium (II)
1,4-diphenyl-1,3-butadiene.

Complexes containing two L groups including bridged complexes
suitable for use in the present invention include:

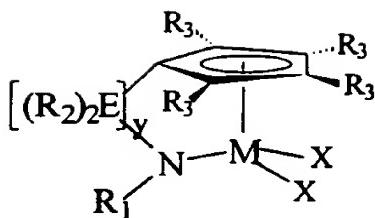
- bis(cyclopentadienyl)zirconiumdimethyl, bis(cyclopentadienyl)zirconium
10 dibenzyl, bis(cyclopentadienyl)zirconium methyl benzyl,
bis(cyclopentadienyl)zirconium methyl phenyl,
bis(cyclopentadienyl)zirconiumdiphenyl, bis(cyclopentadienyl)titanium-allyl,
bis(cyclopentadienyl)zirconiummethyloxide,
bis(cyclopentadienyl)zirconiummethylchloride,
15 bis(pentamethylcyclopentadienyl)zirconiumdimethyl,
bis(pentamethylcyclopentadienyl)titaniumdimethyl,
bis(indenyl)zirconiumdimethyl, indenylfluorenylzirconiumdimethyl,
bis(indenyl)zirconiummethyl(2-(dimethylamino)benzyl),
bis(indenyl)zirconium methyltrimethylsilyl,
20 bis(tetrahydroindenyl)zirconium methyltrimethylsilyl,
bis(pentamethylcyclopentadienyl)zirconiummethylbenzyl,
bis(pentamethylcyclopentadienyl)zirconiumdibenzyl,
bis(pentamethylcyclopentadienyl)zirconiummethyloxide,
bis(pentamethylcyclopentadienyl)zirconiummethylchloride,
25 bis(methylethylcyclopentadienyl)zirconiumdimethyl,
bis(butylcyclopentadienyl)zirconium dibenzyl, bis(t-
butylcyclopentadienyl)zirconiumdimethyl,
bis(ethyltetramethylcyclopentadienyl)zirconiumdimethyl,
bis(methylpropylcyclopentadienyl)zirconium dibenzyl,
30 bis(trimethylsilylcyclopentadienyl)zirconium dibenzyl,

- dimethylsilyl-bis(cyclopentadienyl)zirconiumdimethyl,
dimethylsilyl-bis(tetramethylcyclopentadienyl)titanium-(III) allyl
dimethylsilyl-bis(t-butylcyclopentadienyl)zirconiumdichloride, dimethylsilyl-
bis(n-butylcyclopentadienyl)zirconiumdichloride,
5 (methylene-bis(tetramethylcyclopentadienyl)titanium(III) 2-
(dimethylamino)benzyl, (methylene-bis(n-butylcyclopentadienyl)titanium(III)
2-(dimethylamino)benzyl, dimethylsilyl-bis(indenyl)zirconiumbenzylchloride,
dimethylsilyl-bis(2-methylindenyl)zirconiumdimethyl,
dimethylsilyl-bis(2-methyl-4-phenylinenyl)zirconiumdimethyl,
10 dimethylsilyl-bis(2-methylindenyl)zirconium-1,4-diphenyl-1,3-butadiene,
dimethylsilyl-bis(2-methyl-4-phenylinenyl)zirconium (II) 1,4- diphenyl-
1,3-butadiene, dimethylsilyl-bis(tetrahydroindenyl)zirconium(II) 1,4-diphenyl-
1,3-butadiene, dimethylsilyl-bis(fluorenyl)zirconiummethylchloride,
dimethylsilyl-bis(tetrahydrofluorenyl)zirconium bis(trimethylsilyl),
15 (isopropylidene)(cyclopentadienyl)(fluorenyl)zirconiumdibenzyl, and
dimethylsilyl(tetramethylcyclopentadienyl)(fluorenyl)zirconium dimethyl.

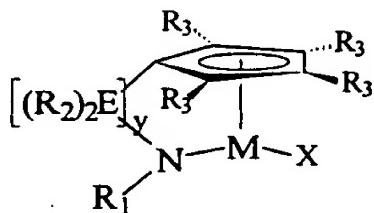
Other catalysts, especially catalysts containing other Group 4 metals, will, of course, be apparent to those skilled in the art.

- Preferred metallocene species for use in the practice of the present invention include constrained geometry metal complexes, including titanium complexes, and methods for their preparation are within the skill in the art as disclosed in U.S. Application Serial No. 545,403, filed July 3, 1990 (EP-A-416,815); U.S. Application Serial No. 967,365, filed October 28, 1992 (EP-A-514,828); and U.S. Application Serial No. 876,268, filed May 1, 1992, (EP-A-520,732), as well as US-A- 5,055,438, US-A- 5,057,475, US-A- 5,096,867, US-A- 5,064,802, US-A-5,096,867, US-A-5,132,380, US-A-5,132,380, US-A-5,470,993, US-A-5,486,632 and US-A- 5,132,380, US-A-5,321,106.

- Especially preferred are metallocene catalysts of Formulas 3, 4, 5, 6, 30 7, 8, 9, 10, 11 or 12, wherein

Formula 3:

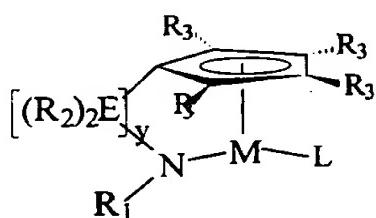
- wherein each X is independently hydrocarbyl, silylhydrocarbyl, including
 5 conjugated diene ligand which coordinates in a metallocyclopentene
 fashion; R₁ is hydrocarbyl or silylhydrocarbyl; E is C or Si; R₂ is
 hydrocarbyl, silylhydrocarbyl or hydrogen; y is 1 or 2; M is a transition
 metal, preferably Hf, Zr or Ti; each R₃ is independently hydrocarbyl or
 silylhydrocarbyl; wherein two adjacent R₃ groups are optionally linked to
 10 form a ring structure, such as an indenyl ligand. These catalysts are
 referred to herein as constrained geometry catalysts in the +4 formal
 oxidation state and are within the skill in the art as illustrated by U.S.
 Patents on constrained geometry catalysts.

Formula 4:

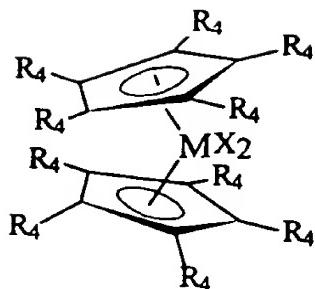
- 15 wherein X is a stabilized hydrocarbyl, or silylhydrocarbyl moiety which is
 optionally further substituted with at least one amine, ether, phosphine, or
 thioether group which is capable of stabilizing the reduced metal center,
 wherein X is optionally an allyl or a hydrocarbyl substituted allyl moiety; R₁
 20 is hydrocarbyl or silylhydrocarbyl; E is C or Si; R₂ is hydrocarbyl or

silylhydrocarbyl or hydrogen; γ is 1 or 2; M is a transition metal, preferably Hf, Zr or Ti; each R₃ is independently hydrocarbyl or silylhydrocarbyl wherein two adjacent R₃ groups are optionally linked to form a ring structure, such an indenyl ligand. These catalysts are referred to herein as 5 constrained geometry catalysts in the +3 formal oxidation state and are within the skill in the art as illustrated by U.S. Patents on constrained geometry catalysts, especially U.S. Patent 5,374,696.

Formula 5:

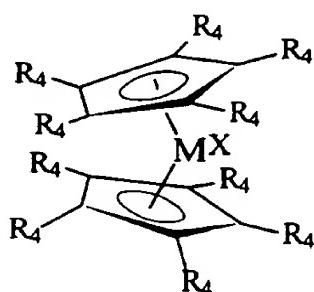


10 wherein L is a conjugated diene ligand bound to the metal center by a π bond; R₁ is hydrocarbyl, or silylhydrocarbyl; E is C or Si; R₂ is hydrocarbyl, silylhydrocarbyl or hydrogen; γ is 1 or 2; M is a transition metal, preferably Zr or Ti; each R₃ is independently hydrocarbyl or silylhydrocarbyl, wherein, two adjacent R₃ groups are optionally linked to form a ring structure, such 15 an indenyl ligand. These catalysts are referred to herein as constrained geometry catalysts in the +2 formal oxidation state and are fully disclosed in U.S. Patent 5,470,993 (Devore et al.).

Formula 6:

wherein X is defined as for Formula 3; M is a transition metal, preferably Zr, Ti or Hf; each R₄ is independently hydrocarbyl or silylhydrocarbyl;

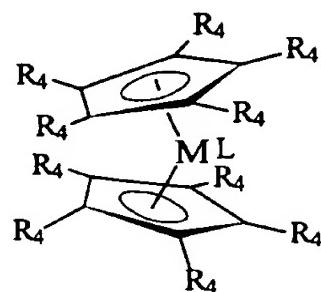
- 5 wherein two adjacent R₄ groups are optionally linked to form a ring structure, such as an indenyl ligand, and wherein an R₄ from one cyclopentadienyl moiety and an R₄ group on a second cyclopentadienyl moiety are optionally linked to form a bridged (or looped) ansa metallocene, as shown below in Formula 9. These catalysts are referred to
- 10 herein as biscyclopentadienyl catalysts in the +4 formal oxidation state and are within the skill in the art as illustrated by U.S. Patents 3,242,099 and 5,198,401.

Formula 7:

- 15 wherein X and M are as defined for Formula 4; and R₄ is as defined for Formula 6. These catalysts are referred to herein as biscyclopentadienyl

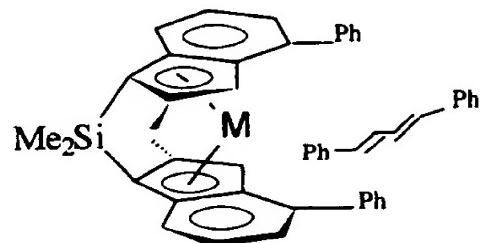
catalysts in the +3 formal oxidation state and are within the skill in the art as illustrated by U.S. Patent 5,374,696 and 5,494,874.

and Formula 8:



- 5 wherein L and M are as defined for Formula 5; and R₄ is as defined for Formula 6. These catalysts are referred to herein as biscyclopentadienyl catalysts in the +2 formal oxidation state and are fully disclosed in PCT Patent Application 96/04290 published February 15, 1996 which corresponds to allowed U.S. Patent Application 481,791 filed June 7,
10 1995.

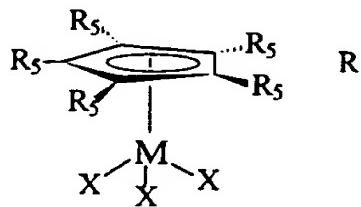
Formula 9:



- wherein L, M and R⁴ are as defined for Formula 8 and each Ph is independently an unsubstituted or inertly substituted phenyl group and each
15 Me is independently an unsubstituted or inertly substituted methyl group; both Ph and Me are preferably unsubstituted. These catalysts are referred to herein as ansa metallocene catalysts and are within the skill in the art as illustrated by PCT Patent Application 96/04290 published February 15,

1996 which corresponds to allowed U.S. Patent Application 481,791 filed June 7, 1995. Such ansa-metallocenes are especially useful in the stereospecific polymerization of prochiral monomers such as propylene.

Formula 10



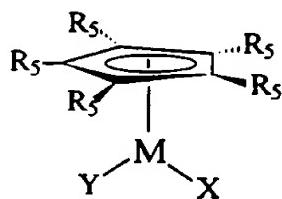
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wherein X is as defined as in Formula 3; M is a transition metal, preferably Hf, Zr or Ti; and each R₅ is independently as defined for R₄ in Formula 6.

These catalysts are referred to herein as monocyclopentadienyl catalysts in the +4 formal oxidation state and are within the skill in the art as

10 illustrated by U.S. Patents 5,064,918; 4,774,301; 5,045,517, and 4,808,680.

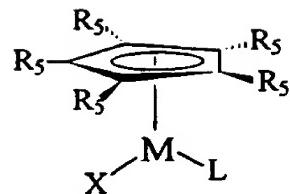
Formula 11



wherein X is defined as in Formula 4; R₅ is as defined for Formula 10; and

15 M is a transition metal preferably Zr, Hf or Ti; Y is an anionic halide, hydrocarbyl, hydrocarbyloxy, dihydrocarbyl, amido or allyl group. These catalysts are referred to herein as monocyclopentadienyl catalysts in the +3 formal oxidation state and are within the skill in the art as illustrated by U.S. Patents 5,374,696 and 5,494,874.

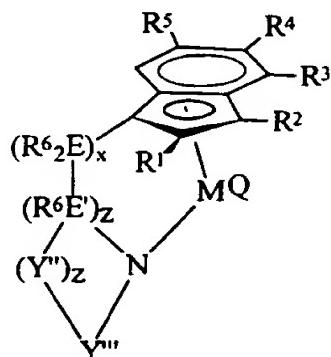
and/or Formula 12



wherein X is as defined in Formula 4; L is as defined in Formula 5; R5 is hydrocarbyl or silylhydrocarbyl wherein two adjacent R5 groups are
 5 optionally linked to form a ring structure, such as an indenyl ligand; and M is a transition metal, preferably Hf, Zr or Ti. These catalysts are referred to herein as monocyclopentadienyl catalysts in the +2 formal oxidation state and are within the skill in the art as disclosed in PCT Patent Application WO 96/00742 corresponding to allowed U.S. Patent Application 267,991 filed
 10 June 28, 1994.

In each formula each hydrocarbyl group is preferably from 1 to 50, more preferably from 1 to 24, most preferably from 1 to 15 non-hydrogen atoms.

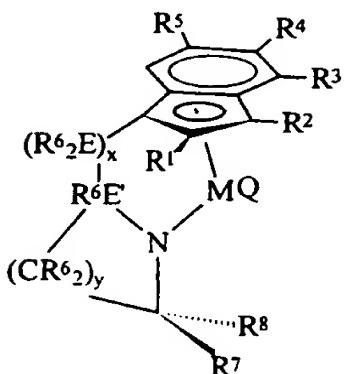
Another preferred family of metallocene catalyst for use in the
 15 practice of the invention is represented by Formula 13:



Formula 13

wherein R¹-R⁶, E, E', M, Q, x and y are as defined for Formulas 14, 15, and 16 hereafter and wherein z, Y'', and Y''' are defined as follows: z = 0 or 1, (1) when z in both occurrences is 1, Y'' is a molecular fragment which is bonded to both E' and Y''' to form a ring and which is selected from (CR⁶)₂, as defined in Formula 14 and Y''' is defined as CR⁷R⁸ as described in Formula 14, or (2) when z in both occurrences is 0, the nitrogen atom is bonded directly to E and (in one embodiment) Y''' is only bonded to N and is defined as CR¹⁰R¹¹R¹² as defined in Formula 15, or (3) (in a second embodiment) when z in both occurrences is 0, Y''' is defined as the 2,4,6-(R¹³)₃C₆H₂ moiety defined in Formula 16. Formula 1A represents compounds which advantageously also correspond to Formula 14, 15, or 16.

Preferred species of Formula 13 include compounds represented by Formula 14:



15

14

wherein M = Ti, Zr, in the +4, +3, or +2 formal oxidation state and Hf in the +4 formal oxidation state. The formal oxidation state depends upon the choice of Q. Preferably, M = Ti or Zr in the +4, +3, or +2 formal oxidation states, more preferably Ti in the +4, +3, or +2 or Zr in the +4 formal oxidation states, most preferably Ti in the +4 or +2 formal oxidation state, particularly Ti in the +2 oxidation state.

- When M is in the + 4 formal oxidation state Q is equal to X_2 , where
 X = halide, hydride, hydrocarbyl (preferably C_{1-20}), hydrocarbyloxy
(preferably C_{1-20}), or dihydrocarbylamide (preferably C_{1-10} for each
hydrocarbyl), independently each occurrence. Alternatively, X_2 together is
5 optionally a conjugated diene (preferably C_{4-40}) which is coordinated in a
metallocyclopentene fashion. Preferably, X_2 = halide, hydrocarbyl (preferably C_{1-6}), hydrocarbyloxy (preferably C_{1-6}), independently each occurrence or X_2 taken together is a conjugated diene (preferably C_{4-20})
ligand coordinated in a metallocyclopentene fashion.
- 10 When M is in the + 3 formal oxidation state Q is equal to X' , where
 X' = 1) a monovalent anionic stabilizing ligand selected from the group
consisting of alkyl, cycloalkyl, aryl, silyl, amido, phosphido, alkoxy, aryloxy,
sulfido groups and mixtures thereof, and being further substituted with an
amine, phosphine, ether, or thioether containing substituent able to form a
15 coordinate-covalent bond or chelating bond with M said ligand having up to
50 non-hydrogen atoms; or 2) a C_{3-10} hydrocarbyl group comprising an
ethylenic unsaturation able to form an η^3 bond with M. Preferred X' ligands
are monovalent anionic stabilizing ligand selected from the group consisting
of alkyl, cycloalkyl, aryl, silyl groups which are being further substituted
with an amine, phosphine, or ether containing substituent able to form a
20 coordinate-covalent bond or chelating bond with M said ligand having up to
30 non-hydrogen atoms; or a hydrocarbyl (preferably C_{3-10}) group
comprising an ethylenic unsaturation able to form an η^3 bond with M. Most
preferred X' ligands are 2-N,N,-dimethylaminobenzyl, allyl, and 1-methyl-
25 allyl.
- When M is in the + 2 formal oxidation state Q is equal to L, where L
= a neutral conjugated diene, optionally substituted with one or more
hydrocarbyl or silylhydrocarbyl groups, said L having up to 40 carbon
atoms and forming a π -complex with M. Preferred L ligands are neutral
30 conjugated dienes, optionally substituted with one or more hydrocarbyl

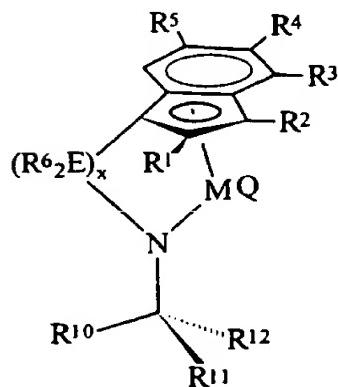
groups, said L having up to 30 carb n atoms and forming a π -complex with M. Most preferred L ligands are 1,4-diphenyl-1,3-butadiene; 1,3-pentadiene; 3-methyl-1,3-pentadiene; 2,4-hexadiene; 1-phenyl-1,3-pentadiene, 1,4-dibenzyl-1,3-butadiene, butadiene, 1,4-ditolyl-
5 1,3-butadiene, 1,4-bis(trimethylsilyl)-1,3-butadiene; said L ligand forming a π -complex with M.

Distinguishing between diene ligands which are π -complexed to M and from those σ -complexed (that is metallocyclopentene) to M is within the skill in the art, for instance as explained in US 5,470,993.

- 10 E = C, Si, Sn, or Ge independently each occurrence, preferably E = C or Si, independently each occurrence. x = 1,2,3, or 4, preferably x = 1, 2, or 3. E' = C, or Si. y = 1, 2, 3, 4, 5, or 6, preferably y = 2 or 3. R¹ = H or hydrocarbyl (preferably C₁₋₁₀), preferably H or hydrocarbyl (preferably C₁₋₆), more preferably methyl (Me). R² = H or hydrocarbyl (preferably C₁₋₁₀), NR⁹₂ (R⁹ = hydrocarbyl (preferably C₁₋₈), independently each occurrence; optionally both R⁹ are coupled to form a ring system), or OR⁹, preferably, H, C₁₋₆ hydrocarbyl, NR⁹₂, more preferably H, phenyl (Ph), or NR⁹₂. R³ = H or hydrocarbyl (preferably C₁₋₁₆), preferably, H or hydrocarbyl (preferably C₁₋₁₂), more preferably alkyl, phenyl, naphthyl,
15 20 hydrocarbyl substituted aryl (preferably of C_{11-C₁₆}) or dialkyl naphthyl, preferably of C₁₂ to C₁₆, most preferably H, phenyl, or 5,8-dimethyl-naphthyl. R⁴, R⁵ = H or C₁₋₈ hydrocarbyl, independently each occurrence; optionally R⁴ and R⁵ are coupled to form a ring system, preferably, H, methyl, or a ring system (hydrocarbyl, substituted or unsubstituted) totaling
25 up to 12 carbon atoms. R⁶ = H or hydrocarbyl (preferably C₁₋₁₆), independently each occurrence; optionally both R⁶ are coupled to form a ring system, preferably hydrocarbyl (preferably C₁₋₁₀), or optionally both R⁶ are coupled to form a ring system, more preferably, methyl, phenyl, or optionally both R⁶ are coupled to form a ring system (hydrocarbyl
30 substituted or unsubstituted) totaling up to 12 carbon atoms. R⁷, R⁸ =

- hydrocarbyl (preferably C₁₋₂₀), optionally both R⁷ and R⁸ are joined to form a ring system; preferably a aromatic (preferably C₁₋₂₀) hydrocarbyl ring system which is either hydrocarbyl substituted or unsubstituted, or both R⁷ and R⁸ may be joined to form a fused aromatic ring system; more
- 5 preferably, phenyl, naphthyl, or both R⁷ and R⁸ are joined to form a fused aromatic ring system.

Other preferred species of compounds or complexes corresponding to Formula 13 include those represented by Formula 15:

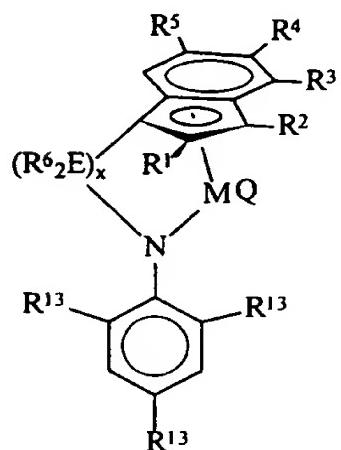


10

15

- wherein M, Q, X, X¹, L, E, x, R¹, R², R⁹, R³, R⁴, R⁵, and R⁶ are as defined for Formula 14 except that R³ is most preferably 5,8-dimethylnaphthyl; and R¹⁰ = H or hydrocarbyl (preferably C₁₋₂₀), preferably H, hydrocarbyl (preferably C₁₋₁₂), more preferably H, phenyl, or methyl. R¹¹, R¹² = independently hydrocarbyl (preferably C₁₋₂₀), independently each occurrence; optionally both R¹¹ and R¹² may be coupled to form a ring system; preferably phenyl, naphthyl, or a coupled aromatic hydrocarbyl ring system (preferably C₁₋₂₀), independently each occurrence; optionally both R¹¹ and R¹² are coupled to form an aromatic hydrocarbyl ring system (hydrocarbyl substituted or unsubstituted) totaling up to 20 carbon atoms.

Further preferred embodiments of Formula 13 include compounds or complexes corresponding to Formula 16:



16

5

wherein M, Q, X, X¹, L, E, x, R¹, R², R⁹, R³, R⁴, R⁵, and R⁶ are as defined for Formula 15; and R¹³ = hydrocarbyl (preferably C₆₋₂₀), preferably aromatic (preferably C₆₋₂₀) hydrocarbyl (hydrocarbyl substituted or unsubstituted), more preferably phenyl, or naphthyl.

- 10 Of the species corresponding to Formulas 13-16 those predicted by modeling to give predominately isotactic insertions of an incoming propylene monomer into a polypropylene chain are preferred, with predictions of higher percentages of isotactic insertions preferred over predictions of lower percentages of isotactic insertions. A method of evaluation to predict isotacticity in polypropylene produced using a catalyst uses the Sybyl force field as calculated by the program SPARTAN (Spartan version 4.1, © 1995 Wavefunction, Inc.) commercially available from Wavefunction, Inc., 18401 Von Karman Ave., #370, Irvine, CA 92715 U.S.A. The initial structure of the species investigated is constructed using the SPARTAN program. In modeling the role of the catalyst in the polymerization, propyl n is the mod 1 for the incoming olefin, and the 2-
- 15
- 20

methylbutyl group models the growing polymer chain directly bonded to the metal. In addition, the midpoint of the olefin double bond is constrained at 2.7 Å away from the metal, to mimic an olefin-catalyst complex prior to the insertion step. The geometries of these species are optimized using the

5 Sybyl force field.

The percentage of isotactic insertions is calculated from the equation:

10 $E_{\text{isotactic}} - E_{\text{syndiotactic}}$ (kcal/mole) @ $\Delta\Delta G = -RT \ln (\%_{\text{isotactic}} / \%_{\text{syndiotactic}})$
where $E_{\text{isotactic}}$ is the computed energy for an isotactic insertion
 $E_{\text{syndiotactic}}$ is the computed energy for a syndiotactic

insertion

$\Delta\Delta G$ is the difference in free energies (ΔG) between the

15 two states

R is the universal gas constant 1.987 cal/mole-K

T is temperature in Kelvin (K)

$\%_{\text{isotactic}}$ is the percentage of expected isotactic insertion

$\%_{\text{syndiotactic}}$ is the percentage of expected syndiotactic

20 insertion

The energies obtained from the Sybyl force field determine the ratio of percentages. The isotactic to syndiotactic ratio (r) (that is % isotactic/%syndiotactic insertions) is calculated at T = 70 °C (343° Kelvin).

25 The percent isotacticity was then calculated from the equation below and compared with the experimental pentad.

$$\%_{\text{isotactic}} = (r/1+r) \times 100$$

$$30 \%_{\text{syndiotactic}} = 100 - \%_{\text{isotactic}}$$

Exemplary of compounds represented by Formulas 14, 15, and 16
are :

- 2,2-di-(2-naphthyl)-6-(2-(η^5 -2-methyl-4-phenyl-indenyl)-ethyl)-piperidinyl
titanium dichloride; 2,2-di-(2-naphthyl)-6-(2-(η^5 -2-methyl-4-phenyl-indenyl)-
5 ethyl)-piperidinyl titanium dimethyl; 2,2-di-(2-naphthyl)-6-(2-(η^5 -2-methyl-4-
phenyl-indenyl)-ethyl)-piperidinyl titanium dimethoxide; 2,2-di-(2-naphthyl)-
6-(2-(η^5 -2-methyl-4-phenyl-indenyl)-ethyl)-piperidinyl titanium diphenyl;
2,2-di-(2-naphthyl)-6-(2-(η^5 -2-methyl-4-phenyl-indenyl)-ethyl)-piperidinyl
titanium dibenzyl; 2,2-di-(2-naphthyl)-6-(2-(η^5 -2-methyl-4-phenyl-indenyl)-
10 ethyl)-piperidinyl titanium bis(dimethylamido); 2,2-di-(2-naphthyl)-6-(2-(η^5 -
2-methyl-4-phenyl-indenyl)-ethyl)-piperidinyl titanium (2-methyl-1,3-
butadiene); 2,2-di-(2-naphthyl)-6-(2-(η^5 -2-methyl-4-phenyl-indenyl)-ethyl)-
piperidinyl titanium 2-N,N,-dimethylaminobenzyl; 2,2-di-(2-naphthyl)-6-(2-(η^5 -2-
15 methyl-4-phenyl-indenyl)-ethyl)-piperidinyl titanium allyl; 2,2-di-(2-
naphthyl)-6-(2-(η^5 -2-methyl-4-phenyl-indenyl)-ethyl)-piperidinyl titanium,
titanium (1,4-diphenyl-1,3-butadiene); 2,2-di-(2-naphthyl)-6-(2-(η^5 -2-
methyl-4-phenyl-indenyl)-ethyl)-piperidinyl titanium (1,3-pentadiene); 2,2-
di-(2-naphthyl)-6-(2-(η^5 -2-methyl-4-phenyl-indenyl)-methyl)-piperidinyl
20 titanium dichloride; 2,2-di-(2-naphthyl)-6-(2-(η^5 -2-methyl-4-phenyl-indenyl)-
-methyl)-piperidinyl titanium dimethyl; 2,2-di-(2-naphthyl)-6-(2-(η^5 -2-
methyl-4-phenyl-indenyl)-methyl)-piperidinyl titanium dimethoxide; 2,2-di-(2-
naphthyl)-6-(2-(η^5 -2-methyl-4-phenyl-indenyl)-methyl)-piperidinyl
25 titanium diphenyl; 2,2-di-(2-naphthyl)-6-(2-(η^5 -2-methyl-4-phenyl-indenyl)-
-methyl)-piperidinyl titanium dibenzyl; 2,2-di-(2-naphthyl)-6-(2-(η^5 -2-methyl-
4-phenyl-indenyl)-methyl)-piperidinyl titanium bis(dimethylamido); 2,2-di-(2-
naphthyl)-6-(2-(η^5 -2-methyl-4-phenyl-indenyl)-methyl)-piperidinyl titanium
30 (2-methyl-1,3-butadiene); 2,2-di-(2-naphthyl)-6-(2-(η^5 -2-methyl-4-phenyl-
indenyl)-methyl)-piperidinyl titanium 2-N,N,-dimethylaminobenzyl; 2,2-di-(2-
naphthyl)-6-(2-(η^5 -2-methyl-4-phenyl-indenyl)-methyl)-piperidinyl titanium
allyl; 2,2-di-(2-naphthyl)-6-(2-(η^5 -2-methyl-4-phenyl-indenyl)-methyl)-

piperidinyl titanium (1,4-diphenyl-1,3-butadiene); 2,2-di-(2-naphthyl)-6-(2-(η^5 -2-methyl-4-phenyl-indenyl)-methyl)-piperidinyl titanium (1,3-pentadiene); 2,2-diphenyl-6-(2-(η^5 -2-methyl-4-phenyl-indenyl)-ethyl)-piperidinyl titanium dichloride; 2,2-diphenyl-6-(2-(η^5 -2-methyl-4-phenyl-indenyl)-ethyl)-
5 piperidinyl titanium dimethyl; 2,2-diphenyl-6-(2-(η^5 -2-methyl-4-phenyl-indenyl)-ethyl)-piperidinyl titanium dimethoxide; 2,2-diphenyl-6-(2-(η^5 -2-methyl-4-phenyl-indenyl)-ethyl)-piperidinyl titanium diphenyl; 2,2-diphenyl-6-(2-(η^5 -2-methyl-4-phenyl-indenyl)-ethyl)-piperidinyl titanium dibenzyl; 2,2-diphenyl-6-(2-(η^5 -2-methyl-4-phenyl-indenyl)-ethyl)-piperidinyl titanium
10 bis(dimethylamido); 2,2-diphenyl-6-(2-(η^5 -2-methyl-4-phenyl-indenyl)-ethyl)-piperidinyl titanium (2-methyl-1,3-butadiene); 2,2-diphenyl-6-(2-(η^5 -2-methyl-4-phenyl-indenyl)-dimethylaminobenzyl; 2,2-diphenyl-6-(2-(η^5 -2-methyl-4-phenyl-indenyl)-ethyl)-piperidinyl titanium allyl; 2,2-diphenyl-6-(2-(η^5 -2-methyl-4-phenyl-indenyl)-ethyl)-piperidinyl titanium (1,4-diphenyl-1,3-butadiene); 2,2-
15 diphenyl-6-(2-(η^5 -2-methyl-4-phenyl-indenyl)-ethyl)-piperidinyl titanium (1,3-pentadiene); as well as the analogous structures wherein at least one of E or E' in Formula 1 is silicon rather than carbon and the R⁶ thereon are independently selected from methyl or phenyl; (9-(9-phenylfluorenyl))amido
20 (η^5 -2-methyl-4-phenyl-indenyl)dimethylsilane titanium dichloride; (9-(9-phenylfluorenyl))amido (η^5 -2-methyl-4-phenyl-indenyl)dimethylsilane titanium dimethyl; (9-(9-phenylfluorenyl))amido (η^5 -2-methyl-4-phenyl-indenyl)dimethylsilane titanium dibenzyl; (9-(9-phenylfluorenyl))amido (η^5 -2-methyl-4-phenyl-indenyl)dimethylsilane titanium dimethoxide; (9-(9-phenylfluorenyl))amido (η^5 -2-methyl-4-phenyl-indenyl)dimethylsilane
25 titanium bis(dimethylamido); (9-(9-phenylfluorenyl))amido (η^5 -2-methyl-4-phenyl-indenyl)dimethylsilane titanium (2-methyl-1,3-butadiene); (9-(9-phenylfluorenyl))amido (η^5 -2-methyl-4-phenyl-indenyl)dimethylsilane titanium 2-N,N,-dimethylaminobenzyl; (9-(9-phenylfluorenyl))amido (η^5 -2-methyl-4-phenyl-indenyl)dimethylsilane titanium allyl; (9-(9-phenylfluorenyl))amido (η^5 -2-methyl-4-phenyl-indenyl)dimethylsilane titanium
30

phenylfluorenlyl)amido (η^5 -2-methyl-4-phenyl-indenyl)dimethylsilane
titanium (1,4-diphenyl-1,3-butadiene); (9-(9-phenylfluorenlyl)amido (η^5 -2-
methyl-4-phenyl-indenyl)dimethylsilane titanium (1,3-pentadiene); (9-(9-
phenylfluorenlyl)amido (η^5 -2-methyl-4-phenyl-indenyl)ethanediyl titanium
5 dichloride; (9-(9-phenylfluorenlyl)amido (η^5 -2-methyl-4-phenyl-indenyl)
ethanediyl titanium dimethyl; (9-(9-phenylfluorenlyl)amido (η^5 -2-methyl-4-
phenyl-indenyl) ethanediyl titanium dibenzyl; (9-(9-phenylfluorenlyl)amido
(η^5 -2-methyl-4-phenyl-indenyl) ethanediyl titanium dimethoxide; (9-(9-
phenylfluorenlyl)amido (η^5 -2-methyl-4-phenyl-indenyl) ethanediyl titanium
10 bis(dimethylamido); (9-(9-phenylfluorenlyl)amido (η^5 -2-methyl-4-phenyl-
indenyl) ethanediyl titanium (2-methyl-1,3-butadiene); (9-(9-
phenylfluorenlyl)amido (η^5 -2-methyl-4-phenyl-indenyl) ethanediyl titanium 2-
N,N,-dimethylaminobenzyl; (9-(9-phenylfluorenlyl)amido (η^5 -2-methyl-4-
phenyl-indenyl) ethanediyl titanium allyl; (9-(9-phenylfluorenlyl)amido (η^5 -2-
15 methyl-4-phenyl-indenyl) ethanediyl titanium (1,4-diphenyl-1,3-butadiene);
(9-(9-phenylfluorenlyl)amido (η^5 -2-methyl-4-phenyl-indenyl) ethanediyl
titanium (1,3-pentadiene); (9-(fluorenlyl)amido (η^5 -2-methyl-4-phenyl-
indenyl)dimethylsilane titanium dichloride; (9-(fluorenlyl)amido (η^5 -2-methyl-
4-phenyl-indenyl)dimethylsilane titanium dimethyl; (9-(fluorenlyl)amido (η^5 -
20 2-methyl-4-phenyl-indenyl)dimethylsilane titanium dibenzyl; (9-
(fluorenlyl)amido (η^5 -2-methyl-4-phenyl-indenyl)dimethylsilane titanium
dimethoxide; (9-(fluorenlyl)amido (η^5 -2-methyl-4-phenyl-
indenyl)dimethylsilane titanium bis(dimethylamido); (9-(fluorenlyl)amido (η^5 -
2-methyl-4-phenyl-indenyl)dimethylsilane titanium (2-methyl-1,3-butadiene);
25 (9-(fluorenlyl)amido (η^5 -2-methyl-4-phenyl-indenyl)dimethylsilane titanium
2-N,N,-dimethylaminobenzyl; (9-(fluorenlyl)amido (η^5 -2-methyl-4-phenyl-
indenyl)dimethylsilane titanium allyl; (9-(fluorenlyl)amido (η^5 -2-methyl-4-
phenyl-indenyl)dimethylsilane titanium (1,-4-diphenyl-1,3-butadiene); (9-
(fluorenlyl)amido (η^5 -2-methyl-4-phenyl-indenyl)dimethylsilane titanium
30 (1,3-pentadiene). (2,4,6-triphenylanilinido)(η^5 -2-methyl-4-phenyl-

- indenyl)dimethylsilane titanium dichloride; (2,4,6-triphenylanilinido)(η^5 -2-methyl-4-phenyl-indenyl)dimethylsilane titanium dimethyl; (2,4,6-triphenylanilinido)(η^5 -2-methyl-4-phenyl-indenyl)dimethylsilane titanium dibenzyl; (2,4,6-triphenylanilinido)(η^5 -2-methyl-4-phenyl-indenyl)dimethylsilane titanium dimethoxide; (2,4,6-triphenylanilinido)(η^5 -2-methyl-4-phenyl-indenyl)dimethylsilane titanium bis(dimethylamido); (2,4,6-triphenylanilinido)(η^5 -2-methyl-4-phenyl-N,N-dimethylaminobenzyl; (2,4,6-triphenylanilinido)(η^5 -2-methyl-4-phenyl-indenyl)dimethylsilane titanium allyl; (2,4,6-triphenylanilinido)(η^5 -2-methyl-4-phenyl-indenyl)dimethylsilane titanium (1,4-diphenyl-1,3-butadiene); (2,4,6-triphenylanilinido)(η^5 -2-methyl-4-phenyl-indenyl)dimethylsilane titanium (1,3-pentadiene); and mixtures thereof.

Tetrahydrocarbyl ammonium salts having a boratabenzene anion are particularly useful in processes involving bulk electrolysis activating techniques. The technique of bulk electrolysis involves the electrochemical oxidation of the metal complex under electrolysis conditions in the presence of a supporting electrolyte comprising a noncoordinating, inert anion, in the practice of the invention a boratabenzene. In the technique, solvents, supporting electrolytes and electrolytic potentials for the electrolysis, are used such that electrolysis byproducts that would render the metal complex catalytically inactive are not substantially formed during the reaction. More particularly, suitable solvents are materials that are liquids under the conditions of the electrolysis (generally temperatures from 0 to 100°C), capable of dissolving the supporting electrolyte, and inert. "Inert solvents" are those that are not reduced or oxidized under the reaction conditions employed for the electrolysis. It is generally possible in view of the desired electrolysis reaction to choose a solvent and a supporting electrolyte that are unaffected by the electrical potential used for the desired electrolysis. Preferred solvents include difluorobenzene (ortho, meta, or para isomers), dimethoxyethane, and mixtures thereof.

The electrolysis is optionally conducted in a standard electrolytic cell containing an anode and cathode (also referred to as the working electrode and counter electrode respectively). Suitable materials of construction for the cell are glass, plastic, ceramic and glass coated metal. The electrodes 5 are prepared from inert conductive materials, by which are meant conductive materials that are unaffected by the reaction mixture or reaction conditions. Platinum or palladium are preferred inert conductive materials. Normally an ion permeable membrane such as a fine glass frit separates the cell into separate compartments, the working electrode compartment and 10 counter electrode compartment. The working electrode is immersed in a reaction medium comprising the metal complex to be activated, solvent, supporting electrolyte, and any other materials desired for moderating the electrolysis or stabilizing the resulting complex. The counter electrode is immersed in a mixture of the solvent and supporting electrolyte. The 15 desired voltage may be determined by theoretical calculations or experimentally by sweeping the cell using a reference electrode such as a silver electrode immersed in the cell electrolyte. The background cell current, the current draw in the absence of the desired electrolysis, is also determined. The electrolysis is completed when the current drops from the 20 desired level to the background level. In this manner, complete conversion of the initial metal complex can be easily detected.

During activation of metallocene complexes by bulk electrolysis the cation of the supporting electrolyte passes to the counter electrode and the boratabenzene anion migrates to the working electrode to become the anion 25 of the resulting oxidized product. Either the solvent or the cation of the supporting electrolyte is reduced at the counter electrode in equal molar quantity with the amount of oxidized metal complex formed at the working electrode.

Use of bulk electrolysis and variations thereon is within the skill in 30 the art as illustrated by U.S. Patents 5,372,682 and 5,425,872.

Advantageous compounds useful as a cocatalyst in one embodiment of the present invention comprise a cation which is a Bronsted acid capable of donating a proton, and an inert, compatible, noncoordinating, boratabenzene anion. Preferred anions are those most capable of balancing

- 5 the charge of the cationic component which is formed when the two components are combined. Also, said anion is preferably sufficiently labile to be displaced by olefinic, diolefinic and acetylenically unsaturated compounds or other neutral Lewis bases such as ethers or nitriles.

Cocatalysts or activators comprising boratabenzenes are used in amounts and under conditions within the skill in the art for other cocatalysts or activators. Their use is applicable to all metallocene catalyzed processes within the skill in the art, including solution, slurry, bulk (especially propylene), and gas phase polymerization processed. Such processes include those fully disclosed in the references cited. Useful monomers to be polymerized include ethylene, propylene, styrene, butene, hexene, pentene, octene and the like.

The molar ratio of catalyst/cocatalyst or activator employed preferably ranges from 1:10,000 to 100:1, more preferably from 1:5000 to 10:1, most preferably from 1:1000 to 1:1. Optionally the cocatalyst is used in combination with a C₃₋₃₀ trihydrocarbyl aluminum compound or oligomeric or polymeric alumoxane. Mixtures of activating cocatalysts may also be employed. It is possible to employ these aluminum compounds for their beneficial ability to scavenge impurities such as oxygen, water, and aldehydes from the polymerization mixture. Preferred aluminum compounds include C₂₋₆ trialkyl aluminum compounds, especially those wherein the alkyl groups are ethyl, propyl, isopropyl, n-butyl, isobutyl, pentyl, neopentyl, or isopentyl, and methyl-alumoxane, modified methylalumoxane and diisobutyl-alumoxane. The molar ratio of aluminum compound to metal complex is preferably from 1:10,000 to 1000:1, more preferably from 1:5000 to 100:1, most preferably from 1:100 to 100:1.

Advantageous addition polymerizable monomers include ethylenically unsaturated monomers, acetylenic compounds, conjugated or non-conjugated dienes, and polyenes. Preferred monomers include olefins, for examples alpha-olefins having from 2 to 20,000, preferably from 2 to 20,

5 more preferably from 2 to 8 carbon atoms and combinations of two or more of such alpha-olefins. Particularly suitable alpha-olefins include, for example, ethylene, propylene, 1-butene, 1-pentene, 4-methylpentene-1, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-undecene, 1-dodecene, 1-tridecene, 1-tetradecene, 1-pentadecene, or combinations

10 thereof, as well as long chain vinyl terminated oligomeric or polymeric reaction products formed during the polymerization, and C₁₀-30 α-olefins specifically added to the reaction mixture in order to produce relatively long chain branches in the resulting polymers. Preferably, the alpha-olefins are ethylene, propene, 1-butene, 4-methyl-pentene-1, 1-hexene, 1-octene, and

15 combinations of ethylene and/or propene with one or more of such other alpha-olefins. Other preferred monomers include styrene, halo- or alkyl substituted styrenes, tetrafluoroethylene, vinylcyclobutene, 1,4-hexadiene, dicyclopentadiene, ethylidene norbornene, and 1,7-octadiene. Mixtures of the above-mentioned monomers may also be employed.

20 In most instances, the polymerization advantageously takes place at conditions known in the prior art for Ziegler-Natta or Kaminsky-Sinn type polymerization reactions, that is, temperatures from 0-250°C and pressures from atmospheric to 3000 atmospheres. Suspension, solution, slurry, gas phase or high pressure, whether employed in batch or continuous form or

25 under other process conditions, including the recycling of condensed monomers or solvent, is optionally employed. Examples of such processes are well known in the art for example, WO 88/02009-A1 or U.S. Patent No. 5,084,534, disclose conditions that are advantageously employed with the polymerization catalysts. A support, especially silica, alumina, or a

30 polymer (especially polytetrafluoroethylen or a polyolefin) is optionally

employed, and desirably is employed when the catalysts are used in a gas phase polymerization process. Such supported catalysts are advantageously not affected by the presence of liquid aliphatic or aromatic hydrocarbons such as are optionally present under the use of condensation techniques in a gas phase polymerization process. Methods for the preparation of supported catalysts are disclosed in numerous references, examples of which are U.S. Patent Nos. 4,808,561, 4,912,075, 5,008,228, 4,914,253, and 5,086,025 and are suitable for the preparation of supported catalysts.

The catalysts are optionally also utilized in combination with at least one additional homogeneous or heterogeneous polymerization catalyst in separate reactors connected in series or in parallel to prepare polymer blends having desirable properties. An example of such a process is disclosed in WO 94/00500, equivalent to U. S. Application Serial Number 10 07/904,770. A more specific process is disclosed in copending application 15 U. S. Application Serial Number 08/10958, filed January 29, 1993.

Use of boratabenzene cocatalysts according to the practice of the invention provides effective cocatalyst or activator activity at lower expense than the prior art of using compounds such as tris(pentafluorophenyl)borane or salts containing tetrakis(pentafluorophenyl)borate which have more of the scarce and difficult to synthesize pentafluorophenyl group per molecule than do the preferred boratabenzenes.

Additionally, boratabenzene cocatalysts are more effective activators than the prior art compounds such as tris(pentafluorophenyl)borane or salts containing tetrakis(pentafluorophenyl)borate in that when a hydrocarbon is abstracted in reactions as illustrated in Figure 1 where a methyl group is removed and methane formed, the reaction is less reversible and recombination is not observed as readily as with the preferred prior art activators and cocatalysts.

The metallocene employed is optionally supported on an inert carrier and optionally or polymerized. Numerous support techniques are known in the art. One technique is employed in accordance with U.S. Pat. No. 5,240,894. Advantageously, the supported metallocene is employed in a 5 prepolymerized fashion. The prepolymer is optionally any alpha olefin, preferably ethylene, propylene, or butene.

The boratabenzene cocatalysts are optionally either chemically bound to a support, for instance by chemically reacting a substituent on the boratabenzene with the support or are evaporated from solution onto a 10 support.

Advantageous inorganic oxide supports for use in the present invention include highly porous silicas, aluminas, aluminosilicates, aluminophosphates, clays, titanias, and mixtures thereof. Preferred inorganic oxides are alumina and silica. The most preferred support material 15 is silica. The support material may be in granular, agglomerated, pelletized, or any other physical form.

Supports advantageous for the present invention preferably have a surface area as determined by nitrogen porosimetry using the B.E.T. method from 10 to 1000 m²/g, and preferably from 100 to 600 m²/g. The pore 20 volume of the support, as determined by nitrogen adsorption, advantageously is between 0.1 and 3 cm³/g, preferably from 0.2 to 2 cm³/g. The average particle size is not critical but typically is from 0.5 to 500 µm, preferably from 1 to 150 µm.

Inorganic oxides, especially silica, alumina and aluminosilicates are 25 known to inherently possess small quantities of hydroxyl functionality attached to the atomic matrix. When used to prepare a reactive component, these materials are preferably first subjected to a heat treatment and/or chemical treatment to reduce the hydroxyl content to 0.001-10 mmole/g, more preferably 0.01-1.0 mmole/g, most preferably 30 0.1-0.8 mmole/g. Advantageous heat treatments (calcining) are carried out

at a temperature from 150 to 900°C, preferably 300 to 850°C for a duration of 10 minutes to 50 hours. Advantageous chemical treatments include contacting with Lewis acid alkylating agents such as trihydrocarbyl aluminum compounds, trihydrocarbylchlorosilane compounds,

- 5 trihydrocarbylalkoxysilane compounds or similar agents. Residual hydroxyl functionality can be detected by the technique of Fourier Transform Infrared Spectroscopy (DRIFTS IR) as disclosed in Fourier Transform Infrared Spectroscopy, P. Griffiths & J. de Haseth, 83 Chemical Analysis, Wiley Interscience (1986), p. 544.

- 10 The inorganic oxide is optionally unfunctionalized except for surface hydroxyl groups as previously disclosed. In this embodiment of the invention the low hydroxyl content of the support leads to superior properties of the resulting supported catalyst, believed to be (but not limited to) lack of interference with the transition metal complex by the residual 15 hydroxyl groups. Preferred hydroxyl contents of such support are less than 0.8 mmole/g, preferably less than 0.5 mmole/g.

The inorganic oxide is optionally also be functionalized by treating with a silane, hydrocarbyloxysilane, or chlorosilane functionalizing agent to attach thereto pendant reactive silane functionality, as previously disclosed.

- 20 Suitable functionalizing agents are compounds that react with the surface hydroxyl groups of the inorganic oxide or react with the metal or metalloid atoms of the inorganic oxide matrix. Examples of advantageous functionalizing agents include phenylsilane, diphenylsilane, methylphenylsilane, dimethylsilane, diethylsilane, diethoxysilane, and 25 chlorodimethylsilane. Techniques for forming such functionalized inorganic oxide compounds were previously disclosed in US Patents 3,687,920 and 3,879,368.

- 30 In a preferred embodiment the silane and the inorganic oxide are contacted, optionally in the presence of a hydrocarbon diluent, in the presence of a base, preferably a C1-4 trialkylamine. The reaction is

conducted at a temperature from 0 to 110°C, preferably from 20 to 50°C. Advantageously an excess of functionalizing agent is employed. Preferred ratios of functionalizing agent based on inorganic oxide are from 1 to 2500 mmole/g. As a result of the foregoing functionalizing reaction, residual 5 hydroxyl functionality of the inorganic oxide is further reduced to the previously mentioned low level of less than 1.0 mmole/g. Preferably, the residual hydroxyl content of functionalized supports is less than 0.8 mmole/g, and most preferably less than 0.5 mmole/g. Highly preferably preparing an advantageous support, a calcined silica is employed having 10 initial (i. e. prefunctionalized) residual hydroxyl content less than 1.0 mmole/g, and from 1 to 20 mmole of functionalizing agent/g silica is employed. The molar ratio of base assist employed to functionalizing agent is advantageously from 0.7:1 to 2.0:1. Unreacted functionalizing agent is preferably removed from the surface of the inorganic oxide, for example, by 15 washing with a liquid hydrocarbon, and the support is preferably thoroughly dried prior to use in preparing supported catalyst systems.

The activator according to the present invention can be linked to a support and corresponds to the Formula 1 or 2 wherein at least one of R' or R" has (comprises, includes or is substituted with) at least one D, a linking 20 group comprising functionality capable of reaction with the support, with and inorganic oxide matrix, thereof, with residual hydroxyl functionality thereof, or with reactive silane functional groups thereon, for example of the optionally functionalized inorganic oxide, or a combination thereof.

Suitable linking substituents, D, used with unmodified inorganic 25 oxides or with inorganic oxide containing only residual hydroxyl functionality, include moieties bearing silane, siloxane, hydrocarbyloxysilane, halosilane, amino, carboxylic acid, carboxylic acid ester, aldehyde, ketone or epoxide functionality, containing from 1 to 1×10^6 nonhydrogen atoms, more preferably from 2 to 1000 nonhydrogen 30 atoms, and most preferably 4 to 20 nonhydrogen atoms. In practice, use of

silane containing compatible anions may require use of a base catalyst, such as a tri(C₁-4 alkyl)amine, to effect the reaction with a substrate containing only residual hydroxyl functionality. Preferably D for use with such unmodified inorganic oxide compounds is a silane or chlorosilane substituted hydrocarbyl radical. Preferred linking substituents, D, include silyl-substituted aryl, silyl-substituted aralkyl, silyl-substituted alkaryl, silyl-substituted alkyl, silyl-substituted haloaryl, or silyl-substituted haloalkyl groups, including polymeric linking groups, most preferably p-silylphenyl (-C₆H₄SiH₃), p-silyltetrafluorophenyl (-C₆F₄SiH₃), silylnaphthyl (-C₁₀H₈SiH₃), silylperfluoronaphthyl (-C₁₀F₈SiH₃), and 2-silyl-1-ethyl-C₂H₄SiH₃), groups.

Advantageous linking substituents, D, used with inorganic oxides that have been modified with reactive silane functionality include moieties bearing silane, siloxane, hydrocarbyloxysilane, halosilane, hydroxyl, thiol, amino, carboxylic acid, carboxylic acid ester, aldehyde, ketone or epoxide functionality containing from 1 to 1x10⁶ nonhydrogen atoms, more preferably from 2 to 1000 nonhydrogen atoms, and most preferably 4 to 20 nonhydrogen atoms. Preferably D, in such circumstances, is a hydroxyl substituted hydrocarbyl radical, more preferably a hydroxy-substituted aryl, hydroxy-substituted aralkyl, hydroxy-substituted alkaryl, hydroxy-substituted alkyl, hydroxy-substituted haloaryl, or hydroxy-substituted haloalkyl group including polymeric linking groups, most preferably hydroxyphenyl, hydroxytolyl, hydroxybenzyl, hydroxynaphthyl, hydroxybisphenyl, hydroxycyclohexyl, C₁-4 hydroxyalkyl, and hydroxy-polystyryl groups, or fluorinated derivatives thereof. A most preferred linking substituent, D, is a p-hydroxyphenyl, 4-hydroxybenzyl, 6-hydroxy-2-naphthyl group, 4-(4'-hydroxyphenyl)phenyl, 4-((4'-hydroxyphenyl)dimethylmethylenephenoxy), or fluorinated derivatives thereof. A base catalyst, such as a tri(C₁-4 alkyl)amine, may also be used to assist in the reaction with the substrate.

Most highly preferably, D is one of the following hydroxy substituted substituents used in combination with a reactive silane functionalized silica.

- Advantageously, the ratio of moles of activator compound to moles of transition metal compound in a supported catalyst is from 0.5:1 to 2:1, 5 preferably from 0.5:1 to 1.5:1 and most preferably from 0.75:1 to 1.25:1. At too low ratios the supported catalyst will not be very active, whereas at too high ratios the catalyst cost becomes excessive due to the relatively large quantities of activator compound utilized. The quantity of transition metal complex chemically bound to the inorganic oxide matrix in the 10 resulting supported catalyst is preferably from 0.0005 to 20 mmole/g, more preferably from 0.001 to 10 mmole/g.

- A supported catalyst can be prepared by combining the support material, the activator compound and the metal complex in any order. Preferably, the inorganic oxide material is first treated with the activator 15 compound by combining the two components in a suitable liquid diluent, such as an aliphatic or aromatic hydrocarbon to form a slurry. The temperature, pressure, and contact time for this treatment are not critical, but generally vary from -20°C to 150°C, from 1 Pa to 10,000 MPa, more preferably at atmospheric pressure (100 kPa), for 5 minutes to 48 hours. 20 Usually the slurry is agitated. After this treatment the solids are typically separated from the diluent.

- Before using the support, the diluent or solvent is preferably removed to obtain a free flowing powder. This is preferably done by applying a technique which only removes the liquid and leaves the resulting solid, such 25 as by applying heat, reduced pressure, evaporation, or a combination thereof. Alternatively, the support is optionally further contacted with the transition metal compound (or metallocene catalyst) prior to removing the liquid diluent. If so contacted the transition metal compound is preferably used dissolved in a suitable solvent, such as a liquid hydrocarbon solvent, 30 advantageously a C₅-10 aliphatic or cycloaliphatic hydrocarbon or a C₆-10

aromatic hydrocarbon. Alternatively, a suspension or dispersion of the transition metal compound in a non-solvent may also be used. The contact temperature is not critical provided it is below the decomposition temperature of the transition metal and of the activator. Good results are obtained in a temperature range of 0 to 100°C. The contact may be total immersion in the liquid medium or contact with an atomized spray of the solution, dispersion or suspension. All steps in the present process should be conducted in the absence of oxygen and moisture. The resulting supported catalyst may be stored or shipped in free flowing form under inert conditions after removal of the solvent.

The supported catalysts of the present invention may be used in addition polymerization processes wherein one or more addition polymerizable monomers are contacted with the supported catalyst of the invention under addition polymerization conditions.

The supported catalyst can be formed *in situ* in the polymerization mixture by introducing into said mixture both a support, or its components, as well as a suitable transition metal compound. The supported catalyst can be advantageously employed in a high pressure, solution, slurry or gas phase polymerization process. A high pressure process is usually carried out at temperatures from 100 to 400°C and at pressures above 500 bar. A slurry process typically uses an inert hydrocarbon diluent and temperatures of from 0°C up to a temperature just below the temperature at which the resulting polymer becomes substantially soluble in the inert polymerization medium. Preferred temperatures are from 40°C to 115°C. The solution process is carried out at temperatures from the temperature at which the resulting polymer is soluble in an inert solvent up to 275°C, preferably at temperatures of from 130°C to 260°C, more preferably from 150°C to 240°C. Preferred inert solvents are C₁-20 hydrocarbons and preferably C₅-10 aliphatic hydrocarbons, including mixtures thereof. The solution and slurry processes are usually carried out at pressures between 100 kPa to 10

MPa. Typical operating conditions for gas phase polymerizations are from 20 to 100°C, more preferably from 40 to 80°C. In gas phase processes the pressure is typically from 10 kPa to 10 MPa. Condensed monomer or diluent may be injected into the reactor to assist in heat removal by means 5 of latent heat of vaporization.

Preferably for use in gas phase polymerization processes, the support has a median particle diameter from 20 to 200 µm, more preferably from 30 µm to 150 µm, and most preferably from 50 µm to 100 µm. Preferably for use in slurry polymerization processes, the support has a median particle 10 diameter from 1 to 200 µm, more preferably from 5 µm to 100 µm, and most preferably from 20 µm to 80 µm. Preferably for use in solution or high pressure polymerization processes, the support has a median particle diameter from 1 to 40 µm, more preferably from 2 µm to 30 µm, and most preferably from 3 µm to 20 µm.

15 In the polymerization process of the present invention, scavengers may be used which serve to protect the supported catalyst from catalyst poisons such as water, oxygen, and polar compounds. These scavengers are generally used in varying amounts depending on the amounts of impurities. Preferred scavengers include the aforementioned 20 organoaluminum compounds of the formula AlR₃ or alumoxanes.

In the present polymerization process, molecular weight control agents can also be used. Examples of such molecular weight control agents include hydrogen, trialkyl aluminum compounds or other known chain transfer agents. A particular benefit of the use of the present supported 25 catalysts is the ability (depending on reaction conditions) to produce narrow molecular weight distribution α-olefin homopolymers and copolymers.

Preferred polymers have M_w/M_n of less than 2.5, more preferably less than 2.3. Such narrow molecular weight distribution polymer products, especially those from a slurry process are highly desirable due to improved 30 tensil strength properties.

The following examples are used to illustrate this invention and not limit it. Ratios, parts, and percentages are by weight unless otherwise stated. Examples (Ex) of the invention are designated numerically while comparative samples (C.S.) are designated alphabetically and are not examples of the invention.

Examples

- 10 For use in the following examples, 1-phenyl-1,4-dihydroboratabenzene and 1-methyl-1,4-dihydroboratabenzene are synthesized following the method described in Herberich, G., et al., *Organometallics*, 1995, 14, 471; Ashe, A., et al., *J. Am. Chem. Soc.*, 1971, 93, 1804; Ashe, A., et al., *J. Am. Chem. Soc.*, 1975, 97, 6865, and references therein. 1-pentafluorophenyl-1,4-dihydroboratabenzene is synthesized in a method analogous to that reported for synthesizing 1-phenyl-boratabenzene in Ashe, *J. Am. Chem. Soc.*, 1971, 93, 1804, except that $C_6F_5BBr_2$ or alternatively $C_6F_5BCl_2$ is used in place of $C_6H_5BBr_2$.
- 15 Lithium salts are synthesized using the method reported for Li[1-phenyl-boratabenzene] in Ashe, *J. Am. Chem. Soc.*, 1971, 93, 1804. Then 1-phenyl-4-methyl-1,4-dihydroboratabenzene is synthesized by reacting the Li[1-phenyl-boratabenzene] with MeI (methyl iodide) in THF (tetrahydrofuran), followed by purification by means within the skill in the art. Li[1-phenyl-4-methyl-boratabenzene] is synthesized analogously, starting with Li[1-pentafluorophenyl-boratabenzene] synthesized analogous to the reported Li[1-phenyl-boratabenzene], but starting with the fluorinated starting material.

- 1,4-pentafluorophenyl-1,4-dihydroboratabenzene is synthesized by reacting Li[1-pentafluorophenyl-boratabenzene] with C₆F₆ in a hydrocarbon or ethereal solvent followed by purification using means within the skill in the art. Then Li[1,4-pentafluorophenyl-boratabenzene] is synthesized
- 5 using the method reported from Li[1-phenyl-boratabenzene] Ashe, Ibid.

Example 1: Polymerization of ethylene and octene using 1-phenyl-1,4-dihydroboratabenzene cocatalyst

- 10 A two liter reactor is charged with 750 g of hydrocarbon solvent commercially available from Exxon Chemicals, Inc. under the trade designation Isopar E™ and 120 g 1-octene comonomer. Hydrogen is added as a molecular weight control agent by differential pressure expansion from a 75 ml addition tank from 300 psig (2070 kPa) to 275 psig (1890 kPa).
- 15 The reactor is heated to the polymerization temperature of 140°C and saturated with ethylene at 500 psig (3450 kPa). 5.00 mmole of (*tert*-butylamido)(*tert*amethyl- η^5 -cyclopentadienyl)dimethylsilane titanium (II) 1,3-pentadiene (0.005 M solution in toluene) is combined with 5 mmole of 1-phenyl-1,4-dihydroboratabenzene (0.005 M solution in toluene) and is
- 20 transferred to a catalyst addition tank. The polymerization is initiated by injecting the contents of the catalyst addition tank into the reactor using high pressure nitrogen. The polymerization conditions are maintained for 10 minutes with ethylene provided on demand at 500 psig, after which the reaction mixture is removed from the reactor and a solid copolymer of
- 25 ethylene and octene is obtained upon removing the volatile compounds from the reaction mixture in a vacuum oven set at 120°C for about 20 hr.

Example 2: Polymerization of ethylene and octene using 1-phenyl-4-methyl-1,4-dihydroboratabenzene cocatalyst

A two liter reactor is charged with 750 g of hydrocarbon solvent
5 commercially available from Exxon Chemicals, Inc. under the trade designation Isopar E™ and 120 g 1-octene comonomer. The reactor is heated to the polymerization temperature of 140°C and saturated with ethylene at 500 psig (3450 kPa). 5.00 mmole of (*tert*-butylamido)(*tert*amethyl- η^5 -cyclopentadienyl)dimethylsilane titanium (IV)
10 dimethyl (0.005 M solution in toluene) is combined with 5 mmole of 1-phenyl-4-methyl-1,4-dihydroboratabenzene (0.005 M solution in toluene) and is transferred to a catalyst addition tank. The polymerization is initiated by injecting the contents of the catalyst addition tank into the reactor using high pressure nitrogen. The polymerization conditions are
15 maintained for 10 minutes with ethylene provided on demand at 500 psig (3450 kPa), after which the reaction mixture is removed from the reactor and a solid copolymer of ethylene and octene is obtained upon removing the volatile compounds from the reaction mixture in a vacuum oven set at 120°C for about 20 hr.

20

Example 3: Polymerization of ethylene and octene using tributylammonium 1,4-pentafluorophenyl-boratabenzene cocatalyst

Synthesis of tributylammonium 1,4-bis(pentafluorophenyl)-boratabenzene

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In an argon atmosphere glovebox, equal molar amounts of tributylammonium chloride and lithium 1,4-bis(pentafluorophenyl)-boratabenzene are reacted in THF overnight. The THF is removed and toluene is added. The slurry is filtered through diatomaceous earth filter aid
30 commercially available from Manville Products Corp. under the trade

designation Celite™ and the residu washed with toluene until the washings are colorless. The filtrate volume is reduced and hexanes are added to precipitate the product. The solid is isolated on a frit, washed two times with 10 ml of hexanes, and dried in vacuo to give a yellow-orange solid.

5 The procedure of Example 1 is followed using 5.00 mmole of (*tert*-butylamido)(*tert*amethyl- η^5 -cyclopentadienyl)dimethylsilane titanium (II) 1,3-pentadiene (0.005 M solution in toluene) in combination with 5 mmole of
10 tributylammonium 1,4- pentafluorophenyl -boratabenzene (0.005 M solution in toluene).

Example 4: Polymerization of ethylene and octene using triphenylcarbenium 1-methyl boratabenzene cocatalyst

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Synthesis of triphenylcarbenium 1-methyl-boratabenzene

In an argon atmosphere glovebox, equal molar amounts of triphenylmethyl chloride and lithium 1-methyl-boratabenzene are slurried in toluene
20 overnight. The toluene is removed and dichloromethane is added. The slurry is filtered through diatomaceous earth filter aid commercially available from Manville Products Corp. under the trade designation Celite™, the filtrate volume is reduced, and hexanes are added to precipitate the product. The solid is isolated on a frit, washed two times with 10 ml of
25 hexanes, and dried in vacuo to give a yellow solid.

Polymerization:

The procedure of Example 2 is followed using 5.00 mmole of (*tert*-butylamido)(tertamethyl- η^5 -cyclopentadienyl)dimethylsilane titanium (IV) dimethyl (0.005 M solution in toluene) in combination with 5 mmole of

- 5 triphenylcarbenium 1-methyl-boratabenzene (0.005 M solution in toluene).

Example 5: Polymerization of ethylene and octene using triethylsilylium 1-phenyl-4-methyl boratabenzene cocatalyst

- 10 Synthesis of triethylsilylium 1-phenyl-4-methyl-boratabenzene

In an argon atmosphere glovebox, triphenylcarbenium 1-phenyl-4-methylboratabenzene is combined with an excess of triethylsilane and stirred overnight at 25°C. The yellow solid is isolated on a frit and washed with

- 15 hexanes to give a yellow-orange solid in nearly quantitative yield.

Polymerization:

The procedure of Example 2 is followed using 5.00 mmole of (*tert*-butylamido)(tertamethyl- η^5 -cyclopentadienyl)dimethylsilane titanium (II) 1,4-diphenyl-1,3-butadiene (0.005 M solution in toluene) in combination with 5 mmole of triethylsilylium 1-phenyl-4-methyl-boratabenzene (0.005 M solution in toluene).

Example 6: Polymerization of propylene using 1-pentafluorophenyl-1,4-

- 25 dihydroboratabenzene cocatalyst

A two liter reactor is charged with 500 ml of hydrocarbon solvent commercially available from Exxon Chemicals, Inc. under the trade designation Isopar E™ and 500 ml of propylene comonomer. Hydrogen is

- 30 added as a molecular weight control agent by differential pressure

expansion from a 75 ml addition tank from 300 psig (2070 kPa) to 275 psig (1890 kPa). The reactor is heated to the polymerization temperature of 70°C. 5.00 mmole of rac-dimethylsilyl-bis(2-methyl-4-phenyl-1-indenyl) zirconium (II) 1,4-diphenyl-1,3-butadiene (0.005 M solution in toluene) is combined with 5 mmole of 1-pentafluorophenyl-1,4-dihydroboratabenzene (0.005 M solution in toluene) and is transferred to a catalyst addition tank. The polymerization is initiated by injecting the contents of the catalyst addition tank into the reactor using high pressure nitrogen. The polymerization conditions are maintained for 15 minutes, after which the reactor is vented and the reaction mixture is removed from the reactor. Solid isotactic polypropylene is obtained upon removing the volatile compounds from the reaction mixture in a vacuum oven set at 120°C for about 20 hr.

15 Example 7: Polymerization of propylene using 1,4-dipentafluorophenyl-1,4-dihydroboratabenzene cocatalyst

A two liter reactor is charged with 500 ml of hydrocarbon solvent commercially available from Exxon Chemicals, Inc. under the trade designation Isopar E™ and 500 ml of propylene comonomer. The reactor is heated to the polymerization temperature of 70°C. 5.00 mmole of rac-dimethylsilyl-bis(2-methyl-4-phenyl-1-indenyl) zirconium (IV) dimethyl (0.005 M solution in toluene) is combined with 5 mmole of 1,4-pentafluorophenyl-1,4-dihydroboratabenzene (0.005 M solution in toluene) and is transferred to a catalyst addition tank. The polymerization is initiated by injecting the contents of the catalyst addition tank into the reactor using high pressure nitrogen. The polymerization conditions are maintained for 15 minutes, after which the reactor is vented and the reaction mixture is removed from the reactor. Solid isotactic polypropylene

is obtained upon removing the volatile compounds from the reaction mixture in a vacuum oven set at 120°C for about 20 hr.

5 Example 8: Polymerization of propylene using tributylammonium 1-pentafluorophenyl-boratabenzene cocatalyst

Synthesis of tributylammonium 1-pentafluorophenyl-boratabenzene

In an argon atmosphere glovebox, equal molar amounts of
10 tributylammonium chloride and lithium 1-pentafluorophenyl-boratabenzene are reacted in THF overnight. The THF is removed and toluene is added. The slurry is filtered through diatomaceous earth filter aid commercially available from Manville Products Corp. under the trade designation Celite™ and the residue washed with toluene until the washings are colorless. The
15 filtrate volume is reduced and hexanes are added to precipitate the product. The solid is isolated on a frit, washed two times with 10 ml of hexanes, and dried in vacuo to give a yellow-orange solid.

Polymerization:

20 The procedure of Example 6 is followed using 5.00 mmole of rac-dimethylsilyl-bis(2-methyl-4-phenyl-1-indenyl) zirconium (II) 1,4-diphenyl-1,3-butadiene (0.005 M solution in toluene) in combination with 5 mmole of tributylammonium 1-pentafluorophenyl-boratabenzene (0.005 M solution in toluene).

25

Example 9: Polymerization of propylene using tributylammonium 1-phenyl-boratabenzene cocatalyst

Synthesis of tributylammonium 1-phenyl-boratabenzene

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In an argon atmosphere glovebox, equal molar amounts of tributylammonium chloride and lithium 1-phenyl-boratabenzene are reacted in THF overnight. The THF is removed and toluene is added. The slurry is filtered through diatomaceous earth filter aid commercially available from

- 5 Manville Products Corp. under the trade designation Celite™ and the residue washed with toluene until the washings are colorless. The filtrate volume is reduced and hexanes are added to precipitate the product. The solid is isolated on a frit, washed two times with 10 ml of hexanes, and dried in vacuo to give a yellow-orange solid.

10

Polymerization:

The procedure of Example 7 is followed using 5.00 mmole of rac-dimethylsilyl-bis(2-methyl-4-phenyl-1-indenyl) zirconium (IV) dimethyl (0.005 M solution in toluene) in combination with 5 mmole of

- 15 tributylammonium 1-phenyl-boratabenzene (0.005 M solution in toluene).

Example 10: Polymerization of propylene using 1-methyl-1,4-dihydroboratabenzene cocatalyst

- 20 The procedure of Example 7 is followed using 5.00 mmole of rac-dimethylsilyl-bis(2-methyl-4-phenyl-1-indenyl) zirconium (II) 1,4-diphenyl-1,3-butadiene (0.005 M solution in toluene) in combination with 5 mmole of 1-methyl-1,4-dihydroboratabenzene (0.005 M solution in toluene).

- 25 Example 11: Polymerization of ethylene and octene using 1-phenyl-1,4-dihydroboratanaphthalene cocatalyst

Synthesis of 1-phenyl-1,4-dihydroboratanaphthalene

To a solution of 1.05 grams (0.005 mol) of di-n-butyltindihydride in TMF

- 30 (20 ml) was added 1.36 grams (0.005 mol) of di-n-butyltindichloride under

- nitrogen. The mixtur was stirred at room temperature for 10 min. 1-Bromo-2-(prop-2-yne)benzene (1.75 grams, 0.009 mole) was added to the mixture and allowed to stir overnight. Lithium (0.14 grams, 0.02 mol) was added and the mixture stirred overnight. After quenching with 5 saturated ammonium chloride, the mixture was extracted with methylene chloride, and the organic layer was dried and concentrated to yield the -1phenyl-1,4-dihydrostannanaphthalene, which is then converted to the corresponding boratanaphthalene by reaction with phenyl boron dichloride, or in an alternative procedure, by reaction with phenyl boron dibromide.
- 10 The procedure of Example 2 is followed using 5.00 mmole of (*tert*-butylamido)(*tert*amethyl- h^5 -cyclopentadienyl)dimethylsilane titanium (II) 1,4-diphenyl-1,3-butadiene (0.005 M solution in toluene) in combination with 5 mmole of 1-phenyl-1,4-dihydroboratanaphthalene (0.005 M solution in 15 toluene).

Example 12: Polymerization of propylene using triphenylcarbenium 1-phenyl-boratanaphthalene cocatalyst

- 20 Synthesis of triphenylcarbenium 1-phenyl-boratanaphthalene
- Lithium 1-phenyl-boratanaphthalene is prepared from 1-phenyl-1,4-dihydroboratanaphthalene analogous to the preparation of Li[1-phenyl-boratabenzene] from 1-phenyl-1,4-dihydroboratabenzene reported by Ashe 25 in J. Am. Chem. Soc., 1971, 93, p. 1804. To prepare the triphenylcarbenium derivative, equal molar amounts of triphenylmethyl chloride and lithium 1-phenyl-boratanaphthalene are slurried in toluene overnight in an argon atmosphere glovebox,. The toluene is removed and dichloromethane is added. The slurry is filtered through diatomaceous 30 earth filter aid commercially available from Manville Products Corp. under

the trade designation C lite™, the filtrate volume is reduced, and hexanes are added to precipitate the product. The solid is isolated on a frit, washed two times with 10 ml of hexanes, and dried in vacuo to give a yellow solid.

- 5 The procedure of Example 7 is followed using 5.00 mmole of rac-dimethylsilyl-bis(2-methyl-4-phenyl-1-indenyl) zirconium (II) 1,4-diphenyl-1,3-butadiene (0.005 M solution in toluene) in combination with 5 mmole of triphenylcarbenium 1-phenyl-boratanaphthalene (0.005 M solution in toluene).

10

Example 13: Synthesis of triphenylcarbenium 1,4-bis(pentafluorophenyl)-boratabenzene

In an argon atmosphere glovebox, equal molar amounts of triphenylmethyl chloride and lithium 1,4-bis(pentafluorophenyl)-boratabenzene are slurried in toluene overnight. The toluene is removed and dichloromethane is added. The slurry is filtered through diatomaceous earth filter aid commercially available from Manville Products Corp. under the trade designation Celite™, the filtrate volume is reduced, and hexanes are added to precipitate the product. The solid is isolated on a frit, washed two times with 10 ml of hexanes, and dried in vacuo to give a yellow solid.

Example 14: Synthesis of 1-phenyl-4-pentafluorophenyl-1,4-dihydro-5,6,7,8 tetrafluoroboratanaphthalene

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The synthetic procedure of Example 11 is repeated using 1-bromo-3,4,5,6-tetrafluoro-2(prop-2-pentafluorophenyl-2-yl)benzene as a starting material to produce the corresponding 1-di-n-butyl-1,4-dihydro-4-pentafluorophenyl-5,6,7,8-tetrafluorostannanaphthalene, which is then converted to the

corresponding boratanaphthalene by reaction with phenyl boron dichloride, or in an alternative procedure, by reaction with phenyl boron dibromide.

Additional cocatalysts useful in the practice of the invention are

- 5 synthesized as follows:

Synthesis of triphenylcarbenium 1-phenyl-4-methyl-boratabenzene

In an argon atmosphere glovebox, equal molar amounts of triphenylmethyl
10 chloride and lithium 1- phenyl -4- methyl -boratabenzene are slurried in
toluene overnight. The toluene is removed and dichloromethane is added.
The slurry is filtered through diatomaceous earth filter aid commercially
available from Manville Products Corp. under the trade designation Celite™,
the filtrate volume is reduced, and hexanes are added to precipitate the
15 product. The solid is isolated on a frit, washed two times with 10 ml of
hexanes, and dried in vacuo to give a yellow solid.

Synthesis of triethylsilylium 1-methyl-boratabenzene

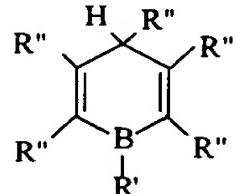
20 In an argon atmosphere glovebox, triphenylcarbenium 1-methyl-
boratabenzene is combined with an excess of triethylsilane and stirred
overnight at 25°C. The solid is isolated on a frit, washed two times with
10 mL of hexanes, and dried in vacuo to give a yellow-orange solid in
nearly quantitative yield.

W claim:

1. A composition of matt or containing an admixture or interaction product of at least one metallocene catalyst or cation thereof and at least one activator comprising a boratabenzene or anion thereof of Formula 1 or

5 2:

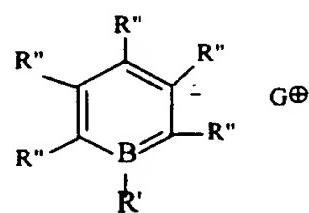
Formula 1



wherein R' is a hydrocarbyl group, silylhydrocarbyl, perfluorohydrocarbyl group, dialkylamido group or halide; the hydrocarbyl group, is linear,

10 branched, cyclic, aromatic, alkyl aromatic, or arylalkyl and is unsubstituted or inertly substituted and has less than 24 carbon atoms; each R'' is independently H, or an unsubstituted or inertly substituted hydrocarbyl, silylhydrocarbyl, perfluorohydrocarbyl, alkoxide or dihydrocarbyl amido group, each as described for R', wherein two or more R'' or R' and at least 15 one R'' are optionally joined into ring or rings which are aromatic, alkyl, or heteroatom rings or combinations thereof; each R' and R'' independently optionally is or comprises D, a linking group; or

Formula 2:



20

wherein R' and R'' are as defined for Formula 1; G+ is a cation.

2. The composition of Claim 1 or 2 wherein the metallocene catalyst is of the formula $L_1MX_mX'_nX_p$, Formula A, or a dimer thereof and the boratabenzene is of Formula 1 or 2.

3. The composition of Claim 1 or 2 wherein the metallocene is a
5 constrained geometry catalyst.

4. The composition of Claim 1 or 2 wherein the metallocene is of Formula 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15 or 16.

5. The composition of Claim 1, 2, 3 or 4 wherein the boratabenzene cocatalyst is of Formula 1 or 2 and R' is aromatic or fluorohydrocarbyl.

10 6. The composition of Claim 8 wherein R' is phenyl, perfluorophenyl, perfluorocarbyl, and at least one R" is H.

7. The composition of Claim 1 or 2 wherein the metallocene catalyst comprises a compound selected from cyclopentadienyltitaniumtrimethyl, cyclopentadienyltitaniumtriethyl, cyclopentadienyltitaniumtriisopropyl,
15 cyclopentadienyltitaniumtriphenyl, cyclopentadienyltitaniumtribenzyl, cyclopentadienyltitanium-2,4-dimethylpentadienyl, cyclopentadienyltitanium-2,4-dimethylpentadienyl-triethylphosphine, cyclopentadienyltitanium-2,4-dimethylpentadienyl-trimethylphosphine, cyclopentadienyltitaniumdimethylmethoxide,
20 cyclopentadienyltitaniumdimethylchloride, pentamethylcyclopentadienyltitaniumtrimethyl, indenyltitaniumtrimethyl, indenyltitaniumtriethyl, indenyltitaniumtripropyl, indenyltitaniumtriphenyl, tetrahydroindenyltitaniumtribenzyl, pentamethylcyclopentadienyltitaniumtriisopropyl,
25 pentamethylcyclopentadienyltitaniumtribenzyl, pentamethylcyclopentadienyltitaniumdimethylmethoxide, pentamethylcyclopentadienyltitaniumdimethylchloride, bis(η^5 -2,4-dimethylpentadienyl)titanium, bis(η^5 -2,4-dimethylpentadienyl)titanium-trimethylphosphine,
30 bis(η^5 -2,4-dimethylpentadienyl)titanium-triethylphosphine,

octahydrofluorenyltitaniumtrimethyl, t trahydroindenyltitaniumtrimethyl,
tetrahydrofluorenyltitaniumtrimethyl, (tert-butylamido)(1,1-dimethyl-
2,3,4,9,10-n-1,4,5,6,7,8-
hexahydronaphthalenyl)dimethylsilanetitaniumdimethyl,
5 (tert-butylamido)(1,1,2,3-tetramethyl-2,3,4,9,10-n-1,4,5,6,7,8-
hexahydronaphthalenyl)dimethylsilanetitaniumdimethyl, (tert-
butylamido)(tetramethyl- η^5 -cyclopentadienyl) dimethylsilanetitanium
dibenzyl, (tert-butylamido)(tetramethyl- η^5 -
cyclopentadienyl)dimethylsilanetitanium dimethyl, (tert-
10 butylamido)(tetramethyl- η^5 -cyclopentadienyl)-1,2-ethanediyltitanium
dimethyl, (tert-butylamido)(tetramethyl- η^5 -indenyl)dimethylsilanetitanium
dimethyl, (tert-butylamido)(tetramethyl- η^5 -cyclopentadienyl)dimethylsilane
titanium (III) 2-(dimethylamino)benzyl; (tert-butylamido)(tetramethyl- η^5 -
cyclopentadienyl)dimethylsilanetitanium (III) allyl, (tert-
15 butylamido)(tetramethyl- η^5 -cyclopentadienyl)dimethylsilanetitanium (III) 2,4-
dimethylpentadienyl, (tert-butylamido)(tetramethyl- η^5 -
cyclopentadienyl)dimethyl-silanetitanium (II) 1,4-diphenyl-1,3-butadiene,
(tert-butylamido)(tetramethyl- η^5 -cyclopentadienyl)dimethyl-silanetitanium
(II) 1,3-pentadiene, (tert-butylamido)(2-methylindenyl)dimethylsilanetitanium
20 (II) 1,4-diphenyl-1,3-butadiene, (tert-butylamido)(2-
methylindenyl)dimethylsilanetitanium (II) 2,4-hexadiene, (tert-butylamido)(2-
methylindenyl)dimethylsilanetitanium (IV) 2,3-dimethyl-1,3-butadiene, (tert-
butylamido)(2-methylindenyl)dimethylsilanetitanium (IV) isoprene,
(tert-butylamido)(2-methylindenyl)dimethylsilanetitanium 1,3-butadiene,
25 (tert-butylamido)(2,3-dimethylindenyl)dimethylsilanetitanium (IV) 2,3-
dimethyl-1,3-butadiene, (tert-butylamido)(2,3-
dimethylindenyl)dimethylsilanetitanium (IV) isoprene, (tert-butylamido)(2,3-
dimethylindenyl)dimethylsilanetitanium (IV) dimethyl, (tert-butylamido)(2,3-
dimethylindenyl)dimethylsilanetitanium (IV) dibenzyl, (tert-butylamido)(2,3-
30 dimethylindenyl)dimethylsilanetitanium 1,3-butadiene, (tert-butylamido)(2,3-

- dimethylindenyl)dimethylsilanetitanium (II) 1,3-pentadiene, (tert-
butylamido)(2,3-dimethylindenyl)dimethylsilanetitanium (II) 1,4-diphenyl-
1,3-butadiene, (tert-butylamido)(2-methylindenyl)dimethylsilanetitanium (II)
1,3-pentadiene, (tert-butylamido)(2-methylindenyl)dimethylsilanetitanium
5 (IV) dimethyl, (tert-butylamido)(2-methylindenyl)dimethylsilanetitanium (IV)
dibenzyl, (tert-butylamido)(2-methyl-4-phenylindenyl)dimethylsilanetitanium
(II) 1,4-diphenyl-1,3-butadiene, (tert-butylamido)(2-methyl-4-
phenylindenyl)dimethylsilanetitanium (II) 1,3-pentadiene, (tert-
butylamido)(2-methyl-4-phenylindenyl)dimethylsilanetitanium (II) 2,4-
10 hexadiene, (tert-butylamido)(tetramethyl- η^5 -cyclopentadienyl)dimethyl-
silanetitanium 1,3-butadiene, (tert-butylamido)(tetramethyl- η^5 -
cyclopentadienyl)dimethyl-silanetitanium (IV) 2,3-dimethyl-1,3-butadiene,
(tert-butylamido)(tetramethyl- η^5 -cyclopentadienyl)dimethyl-silanetitanium
(IV) isoprene, (tert-butylamido)(tetramethyl- η^5 -cyclopentadienyl)dimethyl-
15 silanetitanium (II) 1,4-dibenzyl-1,3-butadiene, (tert-butylamido)(tetramethyl-
 η^5 -cyclopentadienyl)dimethyl- silanetitanium (II) 2,4-hexadiene, (tert-
butylamido)(tetramethyl- η^5 -cyclopentadienyl)dimethyl-silanetitanium (II) 3-
methyl-1,3-pentadiene, (tert-butylamido)(2,4-dimethylpentadien-3-
yl)dimethyl-silanetitaniumdimethyl, (tert-butylamido)(6,6-
20 dimethylcyclohexadienyl)dimethyl-silanetitaniumdimethyl, (tert-
butylamido)(1,1-dimethyl-2,3,4,9,10- η -1,4,5,6,7,8-hexahydronaphthalen-4-
yl)dimethylsilanetitaniumdimethyl, (tert-butylamido)(1,1,2,3-tetramethyl-
2,3,4,9,10- η -1,4,5,6,7,8-hexahydronaphthalen-4-
25 yl)dimethylsilanetitaniumdimethyl(tert-butylamido)(tetramethyl- η^5 -
cyclopentadienyl methylphenyl-silanetitanium (IV) dimethyl,
(tert-butylamido)(tetramethyl- η^5 -cyclopentadienyl methylphenyl-
silanetitanium (II) 1,4-diphenyl-1,3-butadiene, 1-(tert-butylamido)-2-
(tetramethyl- η^5 -cyclopentadienyl)ethanediyl-titanium (IV) dimethyl, and 1-
(tert-butylamido)-2-(tetramethyl- η^5 -cyclopentadienyl)ethanediyl-titanium (II)
30 1,4-diphenyl-1,3-butadiene, bis(cyclopentadienyl)zirconiumdimethyl,

- bis(cyclopentadienyl)zirconium dibenzyl, bis(cyclopentadienyl)zirconium methylbenzyl, bis(cyclopentadienyl)zirconium methylphenyl,
bis(cyclopentadienyl)zirconiumdiphenyl, bis(cyclopentadienyl)titanium-allyl,
bis(cyclopentadienyl)zirconiummethylmethoxide,
- 5 bis(cyclopentadienyl)zirconiummethylchloride,
bis(pentamethylcyclopentadienyl)zirconiumdimethyl,
bis(pentamethylcyclopentadienyl)titaniumdimethyl,
bis(indenyl)zirconiumdimethyl, indenylfluorenylzirconiumdimethyl,
bis(indenyl)zirconiummethyl(2-(dimethylamino)benzyl),
- 10 bis(indenyl)zirconium methyltrimethylsilyl,
bis(tetrahydroindenyl)zirconium methyltrimethylsilyl,
bis(pentamethylcyclopentadienyl)zirconiummethylbenzyl,
bis(pentamethylcyclopentadienyl)zirconiumdibenzyl,
bis(pentamethylcyclopentadienyl)zirconiummethylmethoxide,
- 15 bis(pentamethylcyclopentadienyl)zirconiummethylchloride,
bis(methylethylcyclopentadienyl)zirconiumdimethyl,
bis(butylcyclopentadienyl)zirconium dibenzyl, bis(t-butylcyclopentadienyl)zirconiumdimethyl,
bis(ethyltetramethylcyclopentadienyl)zirconiumdimethyl,
- 20 bis(methylpropylcyclopentadienyl)zirconium dibenzyl,
bis(trimethylsilylcyclopentadienyl)zirconium dibenzyl,
dimethylsilyl-bis(cyclopentadienyl)zirconiumdimethyl,
dimethylsilyl-bis(tetramethylcyclopentadienyl)titanium-(III) allyl
dimethylsilyl-bis(t-butylcyclopentadienyl)zirconiumdichloride, dimethylsilyl-
- 25 bis(n-butylcyclopentadienyl)zirconiumdichloride,
(methylene-bis(tetramethylcyclopentadienyl)titanium(III) 2-(dimethylamino)benzyl, (methylene-bis(n-butylcyclopentadienyl)titanium(III) 2-(dimethylamino)benzyl, dimethylsilyl-bis(indenyl)zirconiumbenzylchloride,
dimethylsilyl-bis(2-methylindenyl)zirconiumdimethyl,
- 30 dimethylsilyl-bis(2-methyl-4-phenylindenyl)zirconiumdimethyl,

dimethylsilyl-bis(2-methylindenyl)zirconium-1,4-diphenyl-1,3-butadiene,
dimethylsilyl-bis(2-methyl-4-phenylindenyl)zirconium (II) 1,4-diphenyl-1,3-
butadiene, dimethylsilyl-bis(tetrahydroindenyl)zirconium(II) 1,4-diphenyl-1,3-
butadiene, dimethylsilyl-bis(fluorenyl)zirconiummethylchloride,
5 dimethylsilyl-bis(tetrahydrofluorenyl)zirconium bis(trimethylsilyl),
(isopropylidene)(cyclopentadienyl)(fluorenyl)zirconiumdibenzyl, and
dimethylsilyl(tetramethylcyclopentadienyl)(fluorenyl)zirconium dimethyl 2,2-
di-(2-naphthyl)-6-(2-(η^5 -2-methyl-4-phenyl-indenyl)-ethyl)-piperidinyl titanium
dichloride; 2,2-di-(2-naphthyl)-6-(2-(η^5 -2-methyl-4-phenyl-indenyl)-ethyl)-piperidinyl
10 titanium dimethyl; 2,2-di-(2-naphthyl)-6-(2-(η^5 -2-methyl-4-phenyl-indenyl)-ethyl)-
piperidinyl titanium dimethoxide; 2,2-di-(2-naphthyl)-6-(2-(η^5 -2-methyl-4-phenyl-
indenyl)-ethyl)-piperidinyl titanium diphenyl; 2,2-di-(2-naphthyl)-6-(2-(η^5 -2-methyl-
4-phenyl-indenyl)-ethyl)-piperidinyl titanium dibenzyl; 2,2-di-(2-naphthyl)-6-(2-(η^5 -
2-methyl-4-phenyl-indenyl)-ethyl)-piperidinyl titanium bis(dimethylamido); 2,2-di-(2-
15 naphthyl)-6-(2-(η^5 -2-methyl-4-phenyl-indenyl)-ethyl)-piperidinyl titanium (2-methyl-
1,3-butadiene); 2,2-di-(2-naphthyl)-6-(2-(η^5 -2-methyl-4-phenyl-indenyl)-ethyl)-
piperidinyl titanium 2-N,N,-dimethylaminobenzyl; 2,2-di-(2-naphthyl)-6-(2-(η^5 -2-
methyl-4-phenyl-indenyl)-ethyl)-piperidinyl titanium allyl; 2,2-di-(2-naphthyl)-6-(2-(η^5 -2-
methyl-4-phenyl-indenyl)-ethyl)-piperidinyl titanium, titanium (1,4-diphenyl-1,3-
butadiene); 2,2-di-(2-naphthyl)-6-(2-(η^5 -2-methyl-4-phenyl-indenyl)-ethyl)-
20 piperidinyl titanium (1,3-pentadiene); 2,2-di-(2-naphthyl)-6-(2-(η^5 -2-methyl-4-phenyl-
indenyl)-methy)-piperidinyl titanium dichloride; 2,2-di-(2-naphthyl)-6-(2-(η^5 -2-
methyl-4-phenyl-indenyl)-methy)-piperidinyl titanium dimethyl; 2,2-di-(2-naphthyl)-
6-(2-(η^5 -2-methyl-4-phenyl-indenyl)-methy)-piperidinyl titanium dimethoxide; 2,2-
25 di-(2-naphthyl)-6-(2-(η^5 -2-methyl-4-phenyl-indenyl)-methy)-piperidinyl titanium
diphenyl; 2,2-di-(2-naphthyl)-6-(2-(η^5 -2-methyl-4-phenyl-indenyl)-methy)-
piperidinyl titanium dibenzyl; 2,2-di-(2-naphthyl)-6-(2-(η^5 -2-methyl-4-phenyl-indenyl)-
-methy)-piperidinyl titanium bis(dimethylamido); 2,2-di-(2-naphthyl)-6-(2-(η^5 -2-
methyl-4-phenyl-indenyl)-methy)-piperidinyl titanium (2-methyl-1,3-butadiene); 2,2-
30 di-(2-naphthyl)-6-(2-(η^5 -2-methyl-4-phenyl-indenyl)-methy)-piperidinyl titanium 2-

N,N,-dimethylaminobenzyl; 2,2-di-(2-naphthyl)-6-(2-(η^5 -2-methyl-4-phenyl-indenyl)-methyl)-piperidinyl titanium allyl; 2,2-di-(2-naphthyl)-6-(2-(η^5 -2-methyl-4-phenyl-indenyl)-methyl)-piperidinyl titanium (1,4-diphenyl-1,3-butadiene); 2,2-di-(2-naphthyl)-6-(2-(η^5 -2-methyl-4-phenyl-indenyl)-methyl)-piperidinyl titanium (1,3-pentadiene); 2,2-diphenyl-6-(2-(η^5 -2-methyl-4-phenyl-indenyl)-ethyl)-piperidinyl titanium dichloride; 2,2-diphenyl-6-(2-(η^5 -2-methyl-4-phenyl-indenyl)-ethyl)-piperidinyl titanium dimethyl; 2,2-diphenyl-6-(2-(η^5 -2-methyl-4-phenyl-indenyl)-ethyl)-piperidinyl titanium dimethoxide; 2,2-diphenyl-6-(2-(η^5 -2-methyl-4-phenyl-indenyl)-ethyl)-piperidinyl titanium diphenyl; 2,2-diphenyl-6-(2-(η^5 -2-methyl-4-phenyl-indenyl)-ethyl)-piperidinyl titanium dibenzyl; 2,2-diphenyl-6-(2-(η^5 -2-methyl-4-phenyl-indenyl)-ethyl)-piperidinyl titanium bis(dimethylamido); 2,2-diphenyl-6-(2-(η^5 -2-methyl-4-phenyl-indenyl)-ethyl)-piperidinyl titanium (2-methyl-1,3-butadiene); 2,2-diphenyl-6-(2-(η^5 -2-methyl-4-phenyl-indenyl)-ethyl)-piperidinyl titanium 2-N,N,-dimethylaminobenzyl; 2,2-diphenyl-6-(2-(η^5 -2-methyl-4-phenyl-indenyl)-ethyl)-piperidinyl titanium allyl; 2,2-diphenyl-6-(2-(η^5 -2-methyl-4-phenyl-indenyl)-ethyl)-piperidinyl titanium (1,4-diphenyl-1,3-butadiene); 2,2-diphenyl-6-(2-(η^5 -2-methyl-4-phenyl-indenyl)-ethyl)-piperidinyl titanium (1,3-pentadiene); as well as the analogous structures wherein at least one of E or E' in Formula 1 is silicon rather than carbon and the R⁶ thereon are independently selected from methyl or phenyl; (9-(9-phenylfluorenly))amido (η^5 -2-methyl-4-phenyl-indenyl)dimethylsilane titanium dichloride; (9-(9-phenylfluorenly))amido (η^5 -2-methyl-4-phenyl-indenyl)dimethylsilane titanium dimethyl; (9-(9-phenylfluorenly))amido (η^5 -2-methyl-4-phenyl-indenyl)dimethylsilane titanium dibenzyl; (9-(9-phenylfluorenly))amido (η^5 -2-methyl-4-phenyl-indenyl)dimethylsilane titanium dimethoxide; (9-(9-phenylfluorenly))amido (η^5 -2-methyl-4-phenyl-indenyl)dimethylsilane titanium bis(dimethylamido); (9-(9-phenylfluorenly))amido (η^5 -2-methyl-4-phenyl-indenyl)dimethylsilane titanium (2-methyl-1,3-butadiene); (9-(9-phenylfluorenly))amido (η^5 -2-methyl-4-phenyl-indenyl)dimethylsilane titanium 2-N,N,-dimethylaminobenzyl; (9-(9-phenylfluorenly))amido (η^5 -2-methyl-4-phenyl-indenyl)dimethylsilane titanium allyl; (9-(9-phenylfluorenly))amido (η^5 -2-methyl-4-

phenyl-indenyl)dimethylsilane titanium (1,4-diphenyl-1,3-butadiene); (9-(9-phenylfluorenyl))amido (η^5 -2-methyl-4-phenyl-indenyl)dimethylsilane titanium (1,3-pentadiene); (9-(9-phenylfluorenyl))amido (η^5 -2-methyl-4-phenyl-indenyl)ethanediyl titanium dichloride; (9-(9-phenylfluorenyl))amido (η^5 -2-methyl-4-phenyl-indenyl)ethanediyl titanium dimethyl; (9-(9-phenylfluorenyl))amido (η^5 -2-methyl-4-phenyl-indenyl)ethanediyl titanium dibenzyl; (9-(9-phenylfluorenyl))amido (η^5 -2-methyl-4-phenyl-indenyl)ethanediyl titanium dimethoxide; (9-(9-phenylfluorenyl))amido (η^5 -2-methyl-4-phenyl-indenyl)ethanediyl titanium bis(dimethylamido); (9-(9-phenylfluorenyl))amido (η^5 -2-methyl-4-phenyl-indenyl)ethanediyl titanium (2-methyl-1,3-butadiene); (9-(9-phenylfluorenyl))amido (η^5 -2-methyl-4-phenyl-indenyl)ethanediyl titanium 2-N,N,-dimethylaminobenzyl; (9-(9-phenylfluorenyl))amido (η^5 -2-methyl-4-phenyl-indenyl)ethanediyl titanium allyl; (9-(9-phenylfluorenyl))amido (η^5 -2-methyl-4-phenyl-indenyl)ethanediyl titanium (1,4-diphenyl-1,3-butadiene); (9-(9-phenylfluorenyl))amido (η^5 -2-methyl-4-phenyl-indenyl)ethanediyl titanium (1,3-pentadiene); (9-(fluorenyl))amido (η^5 -2-methyl-4-phenyl-indenyl)dimethylsilane titanium dichloride; (9-(fluorenyl))amido (η^5 -2-methyl-4-phenyl-indenyl)dimethylsilane titanium dimethyl; (9-(fluorenyl))amido (η^5 -2-methyl-4-phenyl-indenyl)dimethylsilane titanium dibenzyl; (9-(fluorenyl))amido (η^5 -2-methyl-4-phenyl-indenyl)dimethylsilane titanium dimethoxide; (9-(fluorenyl))amido (η^5 -2-methyl-4-phenyl-indenyl)dimethylsilane titanium bis(dimethylamido); (9-(fluorenyl))amido (η^5 -2-methyl-4-phenyl-indenyl)dimethylsilane titanium (2-methyl-1,3-butadiene); (9-(fluorenyl))amido (η^5 -2-methyl-4-phenyl-indenyl)dimethylsilane titanium 2-N,N,-dimethylaminobenzyl; (9-(fluorenyl))amido (η^5 -2-methyl-4-phenyl-indenyl)dimethylsilane titanium allyl; (9-(fluorenyl))amido (η^5 -2-methyl-4-phenyl-indenyl)dimethylsilane titanium (1,-4-diphenyl-1,3-butadiene); (9-(fluorenyl))amido (η^5 -2-methyl-4-phenyl-indenyl)dimethylsilane titanium (1,3-pentadiene). (2,4,6-triphenylanilinido)(η^5 -2-methyl-4-phenyl-indenyl)dimethylsilane titanium dichloride; (2,4,6-triphenylanilinido)(η^5 -2-methyl-4-phenyl-indenyl)dimethylsilane titanium dimethyl; (2,4,6-triphenylanilinido)(η^5 -2-methyl-4-phenyl-indenyl)dimethylsilane titanium dibenzyl; (2,4,6-triphenylanilinido)(η^5 -2-methyl-4-phenyl-

indenyl)dimethylsilane titanium dimethoxide; (2,4,6-triphenylanilinido)(η^5 -2-methyl-4-phenyl-indenyl)dimethylsilane titanium bis(dimethylamido); (2,4,6-triphenylanilinido)(η^5 -2-methyl-4-phenyl-indenyl)dimethylsilane titanium 2-N,N,-dimethylaminobenzyl; (2,4,6-triphenylanilinido)(η^5 -2-methyl-4-phenyl-indenyl)dimethylsilane titanium allyl; (2,4,6-triphenylanilinido)(η^5 -2-methyl-4-phenyl-indenyl)dimethylsilane titanium (1,4-diphenyl-1,3-butadiene); (2,4,6-triphenylanilinido)(η^5 -2-methyl-4-phenyl-indenyl)dimethylsilane titanium (1,3-pentadiene); and mixtures thereof.

8. A composition of matter comprising an anion of Formula 2
10 wherein R' is a pentafluorophenyl group and at least one R" is H.

9. A composition of Claim 1 or 8 comprising
pentafluorophenylboratabenzene, [C₅H₆B-C₆F₅] or
pentafluorophenylboratabenzene anions, [C₅H₅B-C₆F₅]⁻.

10. A composition of matter comprising a boratabenzene of Formula 1 or 2 wherein at least two R" are joined into at least one ring, a boratanaphthalene, a 5,6,7,8-tetrafluoroboratanaphthalene, is a 1-phenylboratanaphthalene or a 1-phenyl-1,4-dihydroboratanaphthalene.

11. A composition of matter formed by the interaction of an alumoxane or aluminum trialkyl, AlR₃ wherein each R is an alkyl group with 20 a metallocene catalyst in the dihalide or dialkyl form followed by addition of a boratabenzene of Formula 1 or 2.

12. A composition of any of Claims 1-11 wherein the boratabenzene is supported on an inert carrier.

13. The composition of Claim 12 wherein boratabenzene cocatalyst 25 is chemically bound or tethered to a support.

14. The composition of Claim 12 or 13 wherein the boratabenzene is of Formula 1 or 2 and at least one of R' or R" has at least one D, a linking group comprising functionality capable reaction with at least one of the support, the inorganic oxide matrix thereof, residual hydroxide

functionality thereof, reactive silane functional group thereon, or a combination thereof.

15. The composition of any of Claims 1-8 or 10-14 wherein the boratabenzene is selected from 1-phenyl-1,4-dihydroboratabenzene; 1-methyl-1,4-dihydroboratabenzene; 1-ethyl-1,4-dihydroboratabenzene; 1-pentafluorophenyl-1,4-dihydroboratabenzene; 1-dimethylamido-1,4-dihydroboratabenzene; 1-neopentyl-1,4-dihydroboratabenzene; 1-tbutyl-1,4-dihydroboratabenzene; 1-trimethylsilyl-1,4-dihydroboratabenzene; 1-trimethylsilylmethyl-1,4-dihydroboratabenzene; 1-fluoro-1,4-dihydroboratabenzene; 1-(3,5-bis-trifluoromethyl-phenyl)-1,4-dihydroboratabenzene; 1-phenyl-4-methyl-1,4-dihydroboratabenzene; 1-ethyl-4-methyl-1,4-dihydroboratabenzene; 1-pentafluorophenyl-4-methyl-1,4-dihydroboratabenzene; 1-dimethylamido-4-methyl-1,4-dihydroboratabenzene; 1-neopentyl-4-methyl-1,4-dihydroboratabenzene; 1-tbutyl-4-methyl-1,4-dihydroboratabenzene; 1-trimethylsilyl-4-methyl-1,4-dihydroboratabenzene; 1-trimethylsilylmethyl-4-methyl-1,4-dihydroboratabenzene; 1-fluoro-4-methyl-1,4-dihydroboratabenzene; 1-(3,5-bis-trifluoromethyl-phenyl)-4-methyl-1,4-dihydroboratabenzene; 1-phenyl-4-tbutyl-1,4-dihydroboratabenzene; 1-methyl-4-tbutyl-1,4-dihydroboratabenzene; 1-ethyl-4-tbutyl-1,4-dihydroboratabenzene; 1-pentafluorophenyl-4-tbutyl-1,4-dihydroboratabenzene; 1-dimethylamido-4-tbutyl-1,4-dihydroboratabenzene; 1-neopentyl-4-tbutyl-1,4-dihydroboratabenzene; 1-tbutyl-4-tbutyl-1,4-dihydroboratabenzene; 1-trimethylsilyl-4-tbutyl-1,4-dihydroboratabenzene; 1-trimethylsilylmethyl-4-tbutyl-1,4-dihydroboratabenzene; 1-fluoro-4-tbutyl-1,4-dihydroboratabenzene; 1-(3,5-bis-trifluoromethyl-phenyl)-4-tbutyl-1,4-dihydroboratabenzene; 1-phenyl-2,4-dimethyl-1,4-dihydroboratabenzene; 1,2,4-trimethyl-1,4-dihydroboratabenzene; 1-ethyl-2,4-dimethyl-1,4-dihydroboratabenzene; 1-pentafluorophenyl-2,4-dimethyl-1,4-

- dihydroboratabenzene; 1-dimethylamido-2,4-dimethyl-1,4-
- dihydroboratabenzene; 1-neopentyl-2,4-dimethyl-1,4-
- dihydroboratabenzene; 1-tbutyl-2,4-dimethyl-1,4-dihydroboratabenzene;
- 1-trimethylsilyl-2,4-dimethyl-1,4-dihydroboratabenzene; 1-
- 5 trimethylsilylmethyl-2,4-dimethyl-1,4-dihydroboratabenzene; 1-fluoro-2,4-dimethyl-1,4-dihydroboratabenzene; 1-(3,5-bis-trifluoromethyl-phenyl)-2,4-dimethyl-1,4-dihydroboratabenzene; 1-phenyl-2-methoxide-4-tbutyl-1,4-dihydroboratabenzene; 1-methyl-2-methoxide-4-tbutyl-1,4-dihydroboratabenzene; 1-ethyl-2-methoxide-4-tbutyl-1,4-
- 10 dihydroboratabenzene; 1-pentafluorophenyl-2-methoxide-4-tbutyl-1,4-dihydroboratabenzene; 1-dimethylamido-2-methoxide-4-tbutyl-1,4-dihydroboratabenzene; 1-neopentyl-2-methoxide-4-tbutyl-1,4-dihydroboratabenzene; 1-tbutyl-2-methoxide-4-tbutyl-1,4-dihydroboratabenzene; 1-trimethylsilyl-2-methoxide-4-tbutyl-1,4-
- 15 dihydroboratabenzene; 1-trimethylsilylmethyl-2-methoxide-4-tbutyl-1,4-dihydroboratabenzene; 1-fluoro-2-methoxide-4-tbutyl-1,4-dihydroboratabenzene; 1-(3,5-bis-trifluoromethyl-phenyl)-2-methoxide-4-tbutyl-1,4-dihydroboratabenzene; 1-phenyl-4-tbutyl-6-trimethylsilyl-1,4-dihydroboratabenzene; 1-methyl-4-tbutyl-6-trimethylsilyl-1,4-
- 20 dihydroboratabenzene; 1-ethyl-4-tbutyl-6-trimethylsilyl-1,4-dihydroboratabenzene; 1-pentafluorophenyl-4-tbutyl-6-trimethylsilyl-1,4-dihydroboratabenzene; 1-dimethylamido-4-tbutyl-6-trimethylsilyl-1,4-dihydroboratabenzene; 1-neopentyl-4-tbutyl-6-trimethylsilyl-1,4-dihydroboratabenzene; 1-tbutyl-4-tbutyl-6-trimethylsilyl-1,4-
- 25 dihydroboratabenzene; 1-trimethylsilyl-4-tbutyl-6-trimethylsilyl-1,4-dihydroboratabenzene; 1-trimethylsilylmethyl-4-tbutyl-6-trimethylsilyl-1,4-dihydroboratabenzene; 1-fluoro-4-tbutyl-6-trimethylsilyl-1,4-dihydroboratabenzene; 1-(3,5-bis-trifluoromethyl-phenyl)-4-tbutyl-6-trimethylsilyl-1,4-dihydroboratabenzene; 1-phenyl-2-diethylamido-4-tbutyl-1,4-
- 30 1,4-dihydroboratabenzene; 1-methyl-2-diethylamido-4-tbutyl-1,4-

- dihydroboratabenzene; 1-ethyl-2-diethylamido-4-^tbutyl-1,4-dihydroboratabenzene; 1-pentafluorophenyl-2-diethylamido-4-^tbutyl-1,4-dihydroboratabenzene; 1-dimethylamido-2-diethylamido-4-^tbutyl-1,4-dihydroboratabenzene; 1-neopentyl-2-diethylamido-4-^tbutyl-1,4-
- 5 dihydroboratabenzene; 1-^tbutyl-2-diethylamido-4-^tbutyl-1,4-dihydroboratabenzene; 1-trimethylsilyl-2-diethylamido-4-^tbutyl-1,4-dihydroboratabenzene; 1-trimethylsilylmethyl-2-diethylamido-4-^tbutyl-1,4-dihydroboratabenzene; 1-fluoro-2-diethylamido-4-^tbutyl-1,4-dihydroboratabenzene; 1-(3,5-bis-trifluoromethyl-phenyl)-2-diethylamido-4-
- 10 ^tbutyl-1,4-dihydroboratabenzene; 1-phenyl-4-pentafluorophenyl-1,4-dihydroboratabenzene; 1-methyl-4-pentafluorophenyl-1,4-dihydroboratabenzene; 1-ethyl-4-pentafluorophenyl-1,4-dihydroboratabenzene; 1-4-bispentafluorophenyl-1,4-dihydroboratabenzene; 1-dimethylamido-4-pentafluorophenyl-1,4-
- 15 dihydroboratabenzene; 1-neopentyl-4-pentafluorophenyl-1,4-dihydroboratabenzene; 1-^tbutyl-4-pentafluorophenyl-1,4-dihydroboratabenzene; 1-trimethylsilyl-4-pentafluorophenyl-1,4-dihydroboratabenzene; 1-trimethylsilylmethyl-4-pentafluorophenyl-1,4-dihydroboratabenzene; 1-fluoro-4-pentafluorophenyl-1,4-
- 20 dihydroboratabenzene; and 1-(3,5-bis-trifluoromethyl-phenyl)-4-pentafluorophenyl-1,4-dihydroboratabenzene, mixtures thereof, and anions thereof.

16. The composition of any of Claims 1-6 or 10-15 wherein the metallocene comprises a transition metal in the + 2 formal oxidation state.

- 25 17. The composition of any of Claims 1-16 wherein the boratabenzene is an anion having the carbon G + and G + is selected from a cation of an ionic activator, $[NHR_3]^+$, $[NR_4]^+$, $[SiR_3]^+$, $[CPh_3]^+$, $[(C_5H_5)_2Fe]^+$, Ag^+ , where R is independently in each occurrence a hydrocarbyl, silylhydrocarbyl, or perfluorocarbyl of from 1 to 24 carbons, and Ph is phenyl; $[NH(CH_3)(C_{18}H_{37})_2]^+$ or a combination thereof.

**18. A process of polymerizing at least one olefin in the presence of
at least one composition of any of Claims 1-17.**

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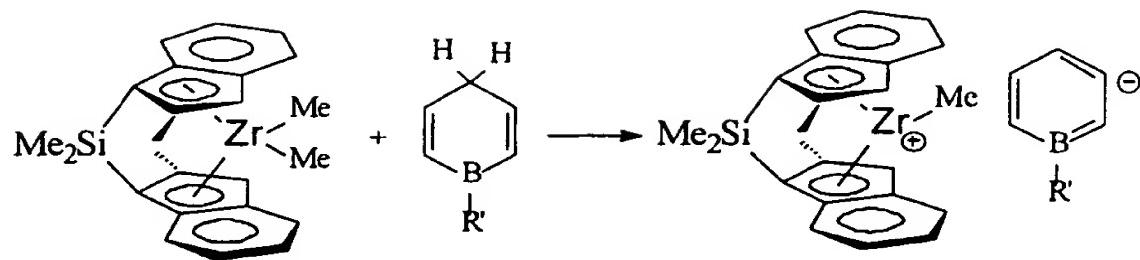


Figure 1

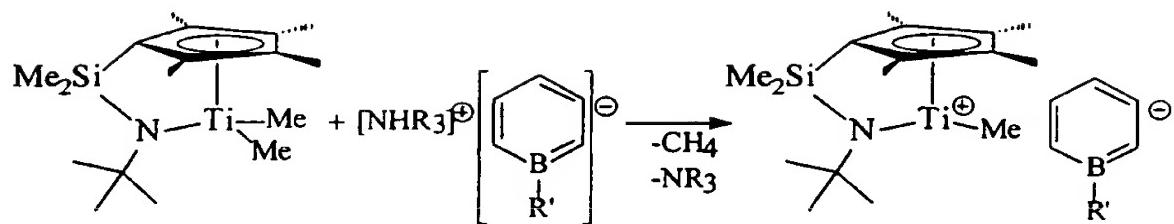


Figure 2

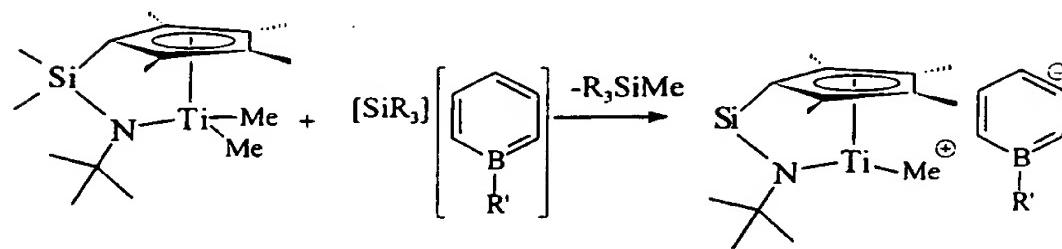


Figure 3

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 97/04247

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08F4/603 C08F10/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO 96 23004 A (OCCIDENTAL CHEMICAL CORPORATION) 1 August 1996 see claim 1 see page 7, line 15 - page 8, line 10 see examples 1-17 -----	1

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

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- 'O' document referring to an oral disclosure, use, exhibition or other means
- 'P' document published prior to the international filing date but later than the priority date claimed

'T' later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

'X' document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

'Y' document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

'&' document member of the same patent family

1

Date of the actual completion of the international search

19 June 1997

Date of mailing of the international search report

04.07.97

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INTERNATIONAL SEARCH REPORT

Information on patent family members

Int'l Application No

PCT/US 97/04247

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9623004 A	01-08-96	US 5554775 A AU 4524396 A US 5637659 A	10-09-96 14-08-96 10-06-97
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